SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,

INCLUDING PAINTS AND PAINT MATERIALS, INKS, LUBRICATING OILS, SOAPS, ETC.

By

PERCY H. WALKER,

CHIEF, CONTRACTS LABORATORY.

ORGANIZATION OF THE BUREAU OF CHEMISTRY.

H. W. WILEY, *Chemist and Chief of Bureau.*
W. D. BIGELOW, *Assistant Chief of Bureau.*
F. L. DUNLAP, *Associate Chemist.*
F. B. LINTON, *Chief Clerk.*

DIVISION OF FOODS:
    W. D. BIGELOW, *Chief.*
  WASHINGTON FOOD INSPECTION LABORATORY:
    L. M. TOLMAN, *Chief.*
CHIEF FOOD AND DRUG INSPECTOR:
    WALTER G. CAMPBELL.
FOOD AND DRUG INSPECTION LABORATORIES:
    New York, R. E. DOOLITTLE, *Chief.*
    Boston, B. H. SMITH, *Chief.*
    Philadelphia, C. S. BRINTON, *Chief.*
    Chicago, A. L. WINTON, *Chief.*
    New Orleans, C. W. HARRISON, *Chief.*
    San Francisco, R. A. GOULD, *Chief.*
    St. Paul, A. S. MITCHELL, *Chief.*
    Detroit, H. L. SCHULTZ, *Chief.*
    Savannah. [Not appointed.]
    Seattle. [Not appointed.]
    Buffalo, W. L. DUBOIS, *Chief.*
    Kansas City. [Not appointed.]
    Denver, A. E. LEACH, *Chief.*
    Galveston. [Not appointed.]
    Portland, Oreg. [Not appointed.]
    Cincinnati. [Not appointed.]
SUGAR LABORATORY:
    Under the direct supervision of the Chief of Bureau.
DAIRY LABORATORY:
    G. E. PATRICK, *Chief.*
MISCELLANEOUS LABORATORY:
    J. K. HAYWOOD, *Chief.*
DRUG LABORATORY:
    L. F. KEBLER, *Chief.*
CONTRACTS LABORATORY:
    P. H. WALKER, *Chief.*
LEATHER AND PAPER LABORATORY:
    F. P. VEITCH, *Chief.*
MICROCHEMICAL LABORATORY:
    B. J. HOWARD, *Chief.*
SPECIAL INVESTIGATIONS:
  PHYSIOLOGICAL CHEMISTRY—
    Animal physiology, F. C. WEBER, *in charge.*
    Vegetable physiology, J. A. LE CLERC, *in charge.*
  BACTERIOLOGICAL CHEMISTRY—
    G. W. STILES, Jr., *in charge, Washington.*
    M. E. PENNINGTON (food research), *in charge, Philadelphia.*
  ENOLOGICAL CHEMISTRY—
    W. B. ALWOOD, *in charge, Charlottesville, Va.*
  NITROGEN SECTION—
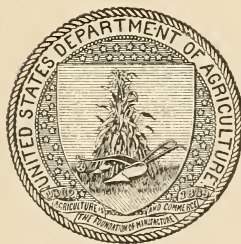   T. C. TRESCOT, *in charge.*

U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF CHEMISTRY—BULLETIN No. 109.

H. W. WILEY, Chief of Bureau.

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,

INCLUDING PAINTS AND PAINT MATERIALS, INKS, LUBRICATING OILS, SOAPS, ETC.

By

PERCY H. WALKER,

CHIEF, CONTRACTS LABORATORY.

LETTER OF TRANSMITTAL.

Sir: I have the honor to submit for your inspection and approval the accompanying manuscript on methods of analysis for certain miscellaneous supplies such as are examined in the Contracts Laboratory of this Bureau. The work of testing materials delivered to the Government on contract grows continually in importance, and the wide variation in the nature of the articles received renders the selection of methods for their analysis of peculiar difficulty. It is thought, therefore, that the assembling of these methods, tested by experience and modified accordingly, will be of service to those engaged in similar work.

I recommend the publication of this manuscript as Bulletin No. 109 of the Bureau of Chemistry.

Respectfully,

H. W. Wiley,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

2

CONTENTS.

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, etc.

INTRODUCTION.

The Contracts Laboratory of the Bureau of Chemistry is called upon to examine a great variety of articles purchased by the Government. The character of the examinations made varies to such an extent that it is not possible to outline any general methods which are not subject to more or less variation according to the purpose for which the material is intended.

In this bulletin are assembled methods which have been found useful in a large number of cases. As a general rule these methods, while not original, have been compiled from a variety of sources and modifications introduced when necessary. No attempt has been made, therefore, except in a few cases, to refer to the original source. Acknowledgments, however, are due to the following authorities: Lunge, Lewkowitsch, Rideal, Fernbach, Hall, Parry, Hurst, Low, and many others. Nor has any attempt been made to give all of the methods for the examination of any of the materials mentioned, but only those which have been found most useful in this laboratory.

The methods are presented in this form because of their inaccessibility at present—scattered as they are throughout chemical literature—and because those selected from the mass of material on the subject have been tested in practice and found to be especially satisfactory.

PAINT MATERIALS.

LINSEED OIL.

1. Specific Gravity.

Determine with a pyknometer or spindle at 15.6° C.

2. Viscosity.

Use the Engler method, making the determination at 20° C.

3. Flash Point, Open Cup.

Set a nickel crucible 60 mm in diameter at the top, 40 mm in diameter at the bottom, and 60 mm in height in a hole in the middle of a sheet of asbestos board 200 mm square. The bottom of the crucible should project about 25 mm through the asbestos. Support the asbestos on a tripod and suspend a thermometer reading to 400° C. in degrees in the center of the crucible, so that the

lower end of the thermometer is 10 mm from the bottom of the crucible. Then pour in the oil until its level is 15 mm below the top of the crucible. Place a Bunsen burner below the crucible and regulate the size of flame so that the thermometer rises 9° a minute. As a test flame use an ordinary blowpipe attached to a gas tube. The flame should be about 6 mm long. Begin testing when the temperature of the oil reaches 220° C., and test for every rise of 3°. In applying the test move the flame slowly across the entire width of the crucible immediately in front of the thermometer and 10 mm above the surface of the oil. The flash point is the lowest temperature at which the vapors above the oil flash and then go out.

4. Fire Point.

After noting the temperature at which the oil flashes continue the heating until the vapors catch fire and burn over the surface of the oil. The temperature at which this takes place is the fire point. In determining the flash point note the behavior of the oil. It should not foam or crack on heating. Foaming and cracking are frequently caused by the presence of water.

5. Turbidity.

Note whether the oil is perfectly clear or not.

6. Foots.

Let a liter of the oil stand in a clear glass bottle for eight days, and then note the amount of residue formed. The highest grades of oil show no turbidity or foots by this test. The claim is made that sometimes what would be called foots by the above method is due to the freezing out of fats of rather high melting point. When a sufficient amount of the sample is available heat one portion to 100° C. and set it aside for the determination of foots together with a sample just as it is received.

7. Break.

Heat 50 cc of the oil in a beaker to 300° C. Note whether the oil remains unchanged or " breaks," that is, shows clots of a jelly-like consistency. Note also the odor of the oil after cooling, and by rubbing it on the hands; a small amount of fish oil may be detected in this way.

8. Moisture.

Heat about 5 grams of oil in an oven at 105° for 45 minutes; the loss in weight is considered as moisture. This determination is, of course, not exact, as there is some oxidation. When more accurate determination is desired perform the whole operation in an atmosphere of hydrogen.

9. Ash.

Burn about 20 grams of oil in a porcelain dish and conduct the ashing at as low a temperature as possible. The best oil should contain only a trace of ash. An amount as large as 0.2 per cent would indicate an adulterated or boiled oil. Examine the ash for lead, manganese, and calcium.

10. Drying on Glass.

Coat glass plates 3 by 4 inches with the oils to be examined, expose to air and light, and note when the film ceases to be tacky. A good oil should dry to an elastic coherent film in 3 days. Varying conditions of light, temperature, and moisture have such an influence on drying tests that for comparison of one linseed oil with others all samples must be run at the same time.

11. Drying on Lead Monoxid.

Livache's test calls for precipitated lead, but litharge gives equally good results. Spread about 5 grams of litharge over the flat bottom of an aluminum dish 2.5 inches in diameter and five-eighths of an inch high, weigh the dish and the litharge; distribute as evenly as possible over the litharge 0.5 to 0.7 gram of the oil, weigh exactly, expose to the air and light for 48 hours, weigh, and calculate the gain in weight to percentage based on the original weight of the oil taken.

12. Acid Number.

Weigh 10 grams of oil in a 200 cc Erlenmeyer flask, add 50 cc of neutral alcohol, connect with a reflux air condenser, and heat on a steam bath for half an hour. Remove from the bath, cool, add phenolphthalein, and titrate the free acid with fifth-normal sodium hydroxid. Calculate as the acid number (milligrams of potassium hydroxid to 1 gram of oil). The acid number varies with the age of the oil, and should be less than 8, though when the oil is refined with sulphuric acid it may show a higher acid number. Test for sulphuric acid.

13. Saponification Number.

Weigh from two to three grams of oil in a 200 cc Erlenmeyer flask, add 30 cc of a half-normal alcoholic solution of potassium hydroxid, connect with a reflux air condenser, heat on a steam bath for an hour, then titrate with half-normal sulphuric acid, using phenolphthalein as indicator. Always run two blanks with the alcoholic potash. From the difference between the number of cubic centimeters of acid required by the blanks and the determinations, calculate the saponification number (milligrams of potassium hydroxid to 1 gram of oil). The saponification number should be about 190.

14. Unsaponifiable Matter.

As the saponification varies somewhat in pure oil, it is sometimes advisable to make a direct determination of unsaponifiable matter. Saponify from 5 to 10 grams of oil with alcoholic potassium hydroxid (200 cc of a half-normal solution) for an hour on a steam bath using a reflux condenser. Then remove the condenser and evaporate the alcohol as completely as possible; dissolve the soap in 75 cc of water, transfer to a separatory funnel, cool, shake out with two portions of 50 cc each of gasoline 88° B., wash the gasoline twice with water, evaporate the gasoline, and weigh the unsaponifiable water. The unsaponifiable water in raw linseed oil should be below 1.5 per cent; in boiled oil it is somewhat higher but should be below 2.5 per cent.

15. Iodin Number.

Weigh in a small glass capsule from 0.2 to 0.25 gram of oil, transfer to a 350 cc bottle having a well ground stopper, dissolve the oil in 10 cc of chloro-

form and add 30 cc of Hanus solution; let it stand with occasional shaking for one hour, add 20 cc of a 10 per cent solution of potassium iodid and 150 cc of water, and titrate with standard sodium thiosulphate, using starch as indicator. Blanks must be run each time. From the difference between the amounts of sodium thiosulphate required by the blanks and the determination, calculate the iodin number (centigrams of iodin to 1 gram of oil). The iodin number of raw linseed oil varies from 175 to 193, though Gill states that a pure raw oil may give a value as low as 160. Boiled oil may be very much lower.

Make the Hanus solution by dissolving 13.2 grams of iodin in 1,000 cc of glacial acetic acid which will not reduce chromic acid, and adding 3 cc of bromin.

16. Rosin Oil (Liebermann-Storch Test).

To 20 grams of oil add 50 cc of alcohol, heat on a steam bath for 15 minutes, cool, decant the alcohol, evaporate to dryness, add 5 cc of acetic anhydrid, warm, cool, draw off the acetic anhydrid, and add a drop of sulphuric acid, 1.53 specific gravity. Rosin oil gives a fugitive violet color.

SPIRITS OF TURPENTINE.

1. Color.

The best quality of spirits of turpentine should be water white.

2. Specific Gravity.

Determine the specific gravity with a pyknometer or Westphal balance at 20°C. Pure gum turpentine should have a density between 0.862 and 0.875. Wood turpentine may, however, range from 0.860 to 0.910 or even higher.

3. Distillation.

Connect a distilling flask of 150 cc capacity with a condenser having a thermometer. Introduce 100 cc of turpentine and heat with a Bunsen burner. The boiling point should be about 156°C., and 95 per cent should distil over between 153.5° and 165.5°C.

4. Residue on Evaporation.

Evaporate 10 grams on the steam bath; the residue should be less than 2 per cent.

5. Refraction Index.

Determine with a Zeiss direct reading refractometer at 20° C. The index of refraction for gum turpentine should be from 1.4690 to 1.4740; for wood turpentine, 1.4685 to 1.5150.

6. Action of Sulphuric Acid (Polymerization).

Measure 6 cc of turpentine in a stoppered, thin-walled tube graduated to 0.1 cc (carbon tubes). Place the tube in cold water and pour in slowly a mixture of four parts of strong sulphuric acid and one part of fuming sulphuric acid. Add the acid slowly, and avoid an excessive rise in temperature. Shake the tube so as to mix the turpentine and the acid, add finally about 20 cc of the acid, stopper the tube, mix thoroughly, cool, allow to stand 30 minutes, and note the volume of unpolymerized oil that collects on top of the acid layer. Then let stand for 18 hours and again note the volume. A pure turpentine should show less than 0.3 cc unpolymerized at the end of 30 minutes, and less than 0.5 after 18 hours.

7. Spot Test.

Place a drop on filter paper and allow it to dry at room temperature; it should leave no stain.

8. Flash Point.

Support a crucible, such as is used in determining the flash point of linseed oil, in a vessel of water at 15° to 20°C.; the water should cover about two-thirds of the crucible. Fill the crucible to within about 2 cm of the top with turpentine, insert a thermometer and heat the water bath slowly, 1° per minute. Begin at 37° and test for the flash at each rise of 0.5°. The turpentine should not flash under 40.5° C.

VARNISH.

The methods of analysis for varnish are far from satisfactory. The following method, slightly modified, is one devised by S. S. Voorhees, and while not absolutely satisfactory, is probably the best available.

1. Insoluble Gums.

Weigh 2 grams of the varnish into a weighed 150 cc Erlenmeyer flask, add 2 cc of chloroform, and then 100 cc of 88° B. gasoline; add the gasoline gradually, shaking constantly so as to avoid any precipitation, until 15 cc are added. Allow to stand over night in a cool place. The gums will adhere to the bottom and side of the Erlenmeyer flask; decant into a weighed beaker and wash with a little 88° gasoline. Dry for two hours at 105° C. and weigh as insoluble gums.

2. Soluble Gums and Linoxyn.

Evaporate the gasoline extract and dry the residue for 168 hours at 100° to 105° C., or to constant weight, and weigh. This treatment should convert all linseed oil into linoxyn. Add 15 cc of chloroform and digest over night to dissolve the gums but not the linoxyn. Filter through a wad of absorbent cotton into a weighed beaker, evaporate the chloroform, dry for 2 hours at 105°, and weigh as soluble gums. Linoxyn is obtained by difference from the first weight.

3. Acid Value.

Determine the acid value in the usual way on 10 grams of the varnish. After getting the acid value, decant the alcohol, evaporate, and apply the Liebermann-Storch test for rosin (p. 8).

4. Ash.

Determine the ash on 10 grams (in a porcelain dish). Determine the reaction of ash with litmus paper; if alkaline, test for lime. It is sometimes well to determine lime, a large amount of which indicates rosin.

5. Miscellaneous.

Volatile oils and metals are determined as in the analysis of the vehicle under mixed paints (p. 28).

It is not possible from such an examination as has been described to decide on the value of a varnish for any particular purpose. An examination of the varnish film should always be made. The film is best made by flowing the varnish on glass, and films should be dried in both a horizontal and a vertical position at a uniform temperature, 38° C. Note the time of setting, the appearance, the hardness and toughness of film. Other tests may also be applied.

JAPAN DRIER.

The analysis of Japan drier is conducted in the same way as that of varnish. The following specifications for Japan drier for the Philadelphia and Reading Railroad are given in an article by Job [a] on Practical Testing and Valuation of Japan as follows:

The material desired consists of a pure turpentine hardener and oil drier, conforming to the following:

1st. When equal parts by weight of the Japan and of pure turpentine are thoroughly mixed and poured over a slab of glass, which is then placed nearly vertical at a temperature of 100 degrees Fahrenheit, with a free access of air but not exposed to draft, the coating shall be hard and dry, neither brittle nor sticky, in not exceeding twelve minutes.

2d. When thoroughly mixed with pure raw linseed oil at the ordinary temperature in proportions of 5 per cent by weight of Japan to 95 per cent by weight of raw linseed oil, no curdling shall result, nor any marked separation or settling on standing.

3d. When the above mixture is flowed over a slab of glass, which is then placed nearly vertical at a temperature of 100 degrees Fahrenheit, with free access to air but not exposed to draft, the coating shall dry throughout, neither brittle nor sticky, in not exceeding two hours.

4th. When five cubic centimeters of the Japan are poured into 95 cubic centimeters of pure turpentine at the ordinary temperature, and thoroughly shaken, a clear solution shall result, without residue, on standing one hour.

5th. After evaporation of the turpentine, the solid residue must be hard and tough, and must not " dust " when scratched with a knife.

6th. Benzine or mineral oil of any kind will not be permitted.

This with the following specification of the U. S. Navy Department will furnish a very good basis for an examination of Japan drier:

1. Japan drier must not flash below 105° F. (open tester); must be of the best quality and made from pure kauri gum, pure linseed oil, pure spirits of turpentine, and lead manganese driers, and be free from adulterants and all other foreign materials; must set to touch in from one-fourth to one hour, dry elastic in from 18 to 21 hours at a temperature of 70° F., and must not rub up or powder under friction by the finger. When mixed with pure raw linseed oil in the proportion of 8 parts of oil to 1 part of drier must remain clear for two hours and set to touch in from 6 to 7 hours at a temperature of 70° F.

PAINTS.

STRENGTH TEST.

The strength of pigments does not bear a very close relationship to the chemical composition, hence a quantitative analysis does not necessarily give the information actually desired. For this reason the " strength test " is of great importance. A standard color is usually selected, but in case no standard is used all of a series of similar colors may be compared with one another.

Weigh equal portions of the samples to be tested, and, if available, a standard sample; add to each equal portions of pure zinc oxid, the amount depending upon the character of the color tested (this may vary from 5 to 60 times that of the color). Rub up each mixture on a glass plate or, better, a stone slab, until there is no change in shade on further rubbing. Rate the samples in the order of their depth of tint. White pigments may be rated in a similar way by grinding up each with the same colored pigment, such as Venetian red. With yellows use chrome green or Prussian blue, instead of a white dilutant. Add the same number of drops of raw linseed oil to all samples in grinding for the strength test.

---

[a] Chemical Engineer, 1906, 4: 198–202.

WHITE PIGMENTS.

1. White Lead.

Pure white lead is basic carbonate of lead and should approach the following composition: $2PbCO_3Pb(OH)_2$. It should be completely soluble in acetic acid. Test for barium and calcium by the flame test. Use an iron wire as platinum will be ruined by the lead.

(a) TOTAL LEAD.

Weigh one gram of the sample, moisten with water, dissolve in acetic acid, filter, and wash, ignite, and weigh the insoluble impurities. To the filtrate from the insoluble matter add 25 cc of sulphuric acid (1:1), evaporate and heat until the acetic acid is driven off; cool, dilute to 200 cc with water, allow to stand for 2 hours, filter on a Gooch crucible, wash with 1 per cent sulphuric acid, ignite, and weigh as lead sulphate. Calculate to total lead ($PbSO_4 \times 0.68292 = Pb$), or calculate to basic carbonate of lead (white lead) by multiplying the weight of lead sulphate by 0.85258.

The filtrate from the lead sulphate may be used to test for other metals, though white lead is only rarely adulterated with soluble substances; test, however, for zinc, which may be present as zinc oxid.

Instead of determining the total lead as sulphate it may be determined as lead chromate by precipitating the hot acetic acid solution with potassium dichromate, filtering on a Gooch crucible, igniting at a low temperature, and weighing as lead chromate.

(b) COMPLETE ANALYSIS.

When it is necessary to determine the exact composition of a pure white lead, heat 1 gram of the pigment in a porcelain boat in a current of dry, carbon-dioxid-free air, catching the water in sulphuric acid and calcium chlorid and the carbon dioxid in soda lime or potassium hydroxid (1.27 specific gravity). By weighing the residue of lead monoxid in the boat all the factors for determining the total composition are obtained. Figure the carbon dioxid to lead carbonate ($PbCO_3$), calculate the lead monoxid corresponding to the lead carbonate ($PbCO_3$) and subtract from the total lead monoxid, calculate the remaining lead monoxid to lead hydroxid ($Pb(OH)_2$), calculate the water corresponding to lead hydroxid and subtract from the total water, the remainder being figured as moisture.

This method assumes the absence of acetic acid. Thompson[a] states that acetic acid varies from 0.05 per cent in Dutch process white lead to 0.7 per cent in some precipitated white leads. It is then more accurate to determine the carbon dioxid by evolution; this is especially the case when working with a lead extracted from a paste in oil, as the lead soap and unextracted oil will cause a considerable error by the ignition method. In determining carbon dioxid by the evolution method, liberate the carbon dioxid with dilute nitric acid, have a reflux condenser next to the evolution flask and dry the carbon dioxid with calcium chlorid before absorbing it in the potassium hydroxid bulbs.

(c) ACETIC ACID.

It is sometimes necessary to determine acetic acid. The Navy Department specifications demand that white lead shall not contain " acetate in excess of

---

[a] J. Soc. Chem. Ind., 1905, **24**: 487.

fifteen one-hundredths of 1 per cent of glacial acetic acid." Thompson's method [a] is as follows:

Eighteen grams of the dry white lead are placed in a 500 cc flask. this flask being arranged for connection with a steam supply, and also with an ordinary Liebig condenser. To this white lead is added 40 cc of syrupy phosphoric acid, 18 grams of zinc dust, and about 50 cc of water. The flask containing the material is heated directly and distilled down to a small bulk. Then the steam is passed into the flask until it becomes about half full of condensed water, when the steam is shut off and the original flask heated directly and distilled down to the same small bulk—this operation being conducted twice. The distillate is then transferred to a special flask and 1 cc of syrup phosphoric acid added to ensure a slightly acid condition. The flask is then heated and distilled down to a small bulk—say, 20 cc. Steam is then passed through the flask until it contains about 200 cc of condensed water, when the steam is shut off and the flask heated directly. These operations of direct distillation and steam distillation are conducted until 10 cc of the distillate require but a drop of tenth-normal alkali to produce a change in the presence of phenolphthalein. Then the bulk of the distillate is titrated with tenth-normal sodium hydroxid, and the acetic acid calculated. It will be found very convenient in this titration, which amounts in some cases to 600–700 cc, to titrate the distillate when it reaches 200 cc. and so continue titrating every 200 cc as it distils over.

If the white lead contains appreciable amounts of chlorin it is well to add some silver phosphate to the second distillation flask and not carry the distillation from this flask too far at any time.

The method used by the chemists of the Navy Department is as follows: Weigh 25 grams of white lead in an Erlenmeyer flask, add 75 cc of 25 per cent phosphoric acid, distil with steam to a 500 cc distillate, add to the distillate some milk of barium carbonate, bring to a boil, filter, keeping the solution at the boiling point (it is not necessary to wash), add an excess of sulphuric acid to the filtrate and determine the barium sulphate in the usual manner; subtract 53 milligrams from the weight of the barium sulphate and calculate the remainder as acetic acid ($BaSO_4 \times 0.515 = CH_3COOH$). The object of this rather indirect method is to avoid any error that might arise from fatty acids being carried over by the steam distillation. For white lead that has not been ground in oil. Thompson's method is to be preferred.

2. Lead Zinc Whites.

French zinc is practically pure zinc oxid. being made from metallic zinc. American zinc is made by roasting zinc ores, and almost always contains some lead. Sublimed lead is made by volatilizing galena, and as sphalerite is usually associated with the galena, it nearly always contains zinc oxid in addition to the basic sulphate of lead. Zinc lead is essentially lead sulphate and zinc oxid.

(a) Moisture.

Dry 2 grams for 2 hours at a temperature of 105° C.

(b) Soluble Sulphate.

Boil 1 gram of the sample with 75 cc of water and 25 cc of alcohol. filter, wash with a mixture of alcohol and water (1:3), and determine sulphuric acid in the filtrate by the usual method of precipitation with barium chlorid. The soluble sulphate may be calculated to zinc sulphate.

---

[a] J. Soc. Chem. Ind., 1905, **24**: 487.

(c) Insoluble and Total Sulphate.

Treat 1 gram in a 600 cc beaker with 10 cc of water, 10 cc of strong hydrochloric acid, and 5 grams of ammonium chlorid, heat on a steam bath in a covered beaker for 5 minutes, add hot water to make about 400 cc, boil for 5 minutes, and filter to separate any insoluble material. (A pure color should be completely dissolved.) Wash with hot water, ignite, and weigh the insoluble. To the boiling hot filtrate add slowly, with stirring, 20 cc of a 10 per cent barium chlorid solution; let stand for 2 hours on the steam bath, filter, wash, ignite, and weigh as barium sulphate. Calculate the total sulphate (SO_4), deduct from it the soluble sulphate (SO_4), and figure the remainder as lead sulphate.

(d) Lead and Zinc.

(1) in the absence of other metals.

Dissolve 1 gram by boiling 15 minutes with 250 cc of water and 20 cc of strong nitric acid, add 5 cc of sulphuric acid, evaporate, and heat until all of the nitric acid is driven off and copious fumes of sulphuric anhydrid begin to come off; cool, dilute, filter on a Gooch crucible, wash with 1 per cent sulphuric acid, ignite, and weigh as lead sulphate. Deduct from this the lead sulphate obtained from the sulphate determination and figure the remainder to lead monoxid. Evaporate the filtrate from the lead sulphate to 100 cc, cool, add 5 grams of microcosmic salt dissolved in water, then add ammonium hydroxid until the solution is just neutral (test with litmus paper). Then add 2 drops of ammonium hydroxid and 1 cc of acetic acid, stir vigorously, heat on the steam bath for an hour (the precipitate should assume a crystalline character and settle well at the end of that time), filter on a Gooch crucible, wash with hot water, ignite at first at a very low heat and finally heat to redness, and weigh as zinc pyrophosphate ($Zn_2P_2O_7$), calculate to zinc oxid ($Zn_2P_2O_7 \times 0.53412 = ZnO$). Deduct the zinc oxid present as zinc sulphate and report the remainder as zinc oxid.

(2) in the presence of other metals.

With a sample containing calcium or magnesium salts the lead should be precipitated as sulphid from hydrochloric acid solution, then dissolved in nitric acid and determined as sulphate. The filtrates from the lead sulphid can be used to determine the zinc. If it is desired to make a gravimetric determination of zinc, boil off the hydrogen sulphid, add a little bromin water to oxidize any trace of iron, then add ammonium hydroxid in excess; only in rare cases will any iron appear here, but if it does, filter, redissolve, and reprecipitate. Manganese will be present only very rarely; if present, it can be precipitated by adding bromin and warming. Make the zinc solution acid with acetic acid, heat to a boil, and pass hydrogen sulphid into the hot solution until it is completely saturated (for 20 to 30 minutes). Allow the zinc sulphid to settle for 5 hours, filter, wash with hydrogen sulphid water, dissolve the zinc sulphid in hot dilute hydrochloric acid, boil off the hydrogen sulphid, and determine the zinc as pyrophosphate, as described.

The hydrogen sulphid method is very troublesome on account of the difficulty of filtering and washing zinc sulphid, and when calcium or magnesium are present it is generally better to determine the zinc volumetrically. This is best done by Low's method.[a] In the absence of iron and manganese take the filtrate from the lead sulphid, add ammonium hydroxid until alkaline, then hydrochloric

---

[a] Technical Methods of Ore Analysis, p. 209.

acid until just acid, then add 3 cc of strong hydrochloric acid, dilute to about 250 cc, and titrate with standard ferrocyanid just as in standardizing the solution. When iron and manganese are present follow the method for oxidized ores as described by Low.

(e) STANDARDIZING THE FERROCYANID SOLUTION.

Prepare a solution of potassium ferrocyanid containing 22 grams of the crystallized salt to the liter. Standardize this solution as follows: Weigh carefully about 0.2 gram of pure zinc and dissolve in 10 cc of strong hydrochloric acid (sp. gr. 1.20), using a 400 cc covered beaker. Dilute somewhat, place a bit of litmus paper in the solution as an indicator, and make faintly alkaline with ammonium hydroxid. Again acidify faintly with hydrochloric acid and then add 3 cc excess of the strong acid. Dilute now to about 250 cc and heat nearly to boiling.

Titrate the hot liquid with the ferrocyanid solution as follows: Pour off about one-third of the zinc solution and set it aside in a beaker. Titrate the remainder by running in a few cubic centimeters at a time until a drop, when tested on a porcelain plate with a drop of a 5 per cent solution of uranium nitrate, shows a brown tinge. Now add the greater part of the reserved portion and continue the titration more cautiously until the end-point is again passed. Finally, add the last of the reserved portion, and to save rinsing out the beaker, pour a large part of the solution back into it again and then empty it once more.

Finish the titration very carefully, ordinarily by testing after each addition of two drops. Instead of using a single drop of the zinc solution for the test, the reaction is sharper if a quantity equivalent to several drops is taken. If this is done near the end of the titration the amount of zinc lost thereby will be insignificant. A convenient way of making the test is to use a medicine-dropper and place a single drop of the uranium solution in each depression of the test-plate at the outset. By using a glass tube instead of a rod for a stirrer, any desired quantity of the solution can be quickly removed for a test. When the final brown tinge is obtained, note the reading of the burette, and then wait a minute or two and observe if one or more of the preceding tests do not also develop a color. The end-point is always passed by a test or two and the burette reading must be corrected accordingly. A further correction must also be made for the amount of ferrocyanid required to produce a color under the same conditions when no zinc is present. This is ordinarily 2 drops. One cubic centimeter of the standard solution will equal about 0.005 gram of zinc.

3. Calcium Pigments.

Whiting is calcium carbonate and is used extensively as an adulterant. Plaster of Paris is dehydrated calcium sulphate and gypsum is the natural hydrated calcium sulphate ($CaSO_4+2H_2O$). Besides these a precipitated calcium sulphate is used, especially as a basis upon which to precipitate anilin colors. A microscopic examination is therefore of importance.

Free lime is objectionable and is especially to be looked for in whiting. Boil two grams of the sample for five minutes with 100 cc of water and add phenolphthalein. If red color develops free lime may be assumed to be present, though the alkaline reaction may possibly be due to hydrates of sodium or potassium.

For quantitative analysis, when such is necessary, boil one gram of the sample with 25 cc of hydrochloric acid (1 : 1), add 150 cc of water, boil, filter,

wash, ignite, and weigh the insoluble. Precipitate iron and aluminum hydrates from the filtrate with ammonium hydroxid, dissolve in hydrochloric acid and reprecipitate, wash, ignite, and weigh. Unite the filtrates from the iron and alumina precipitation, heat to boiling, add slowly 25 cc of a boiling solution of ammonium oxalate (the solution should be saturated at room temperature); let stand on the steam bath for one to two hours, filter, wash free from chlorids (cold water is better for washing than hot water), and determine the calcium by igniting to constant weight in a platinum crucible. A blast lamp is generally recommended for this purpose, but if a platinum triangle is used to support the crucible, from 15 to 30 minutes' ignition with a good Bunsen burner will convert the oxalate entirely to oxid with less danger of loss than with a blast. If great accuracy is required it is well to dissolve the calcium oxalate in hydrochloric acid and reprecipitate.

Instead of weighing the calcium as CaO, it may be determined volumetrically by titrating with potassium permanganate as follows: Precipitate as described, and wash free from ammonium oxalate (when free the filtrate will not react for chlorids). Return the moist precipitate to the beaker by washing with a stream of water, remove the small quantity remaining on the paper with hot dilute sulphuric acid, add 20 cc of sulphuric acid (1:1), dilute to 300 cc, heat to about 80° C., and titrate with tenth-normal potassium permanganate (1 cc=0.0028 gram of calcium oxid). Evaporate the filtrate from the calcium oxalate to about 100 cc, make neutral by the addition of hydrochloric acid, if necessary cool in ice water, add an excess of a solution of sodium ammonium phosphate, stir, allow to stand for 15 minutes, then add 20 cc of strong ammonium hydroxid, stir well, allow to stand for 2 hours, filter in a gooch, wash with 2 per cent ammonium hydroxid, ignite gently at first and finally to a bright red, and weigh as magnesium pyrophosphate ($Mg_2P_2O_7$).

4. Barytes.

Barytes, being one of the cheapest white pigments, is seldom adulterated. It should be white and well ground. A miscroscopic examination should be made to determine the evenness of grinding, the size and angularity of the particles, and whether they are amorphous or crystalline.

(a) Moisture.

Dry 2 grams of the sample at 105° C. for 2 hours. The loss in weight represents the moisture.

(b) Insoluble.

Boil 1 gram in hydrochloric acid (1:3), evaporate to dryness, moisten with hydrochloric acid, dilute with water, boil, filter, and wash. If a previous qualitative examination has determined the absence of lead and other easily reduced metals, ignite in platinum, weigh, and calculate the total insoluble; this may generally be safely calculated to barium sulphate ($BaSO_4$), but to determine any silica that may be present add hydrofluoric acid and sulphuric acid, evaporate the acids, ignite, and weigh; calculate the loss as silicon dioxid.

(c) Alumina and Oxids of Iron.

Add ammonium hydroxid to the filtrate from the total insoluble, boil, filter, wash, ignite, and weigh as oxid of iron and alumina.

(d) Lime.

Precipitate with ammonium oxalate from the filtrate from oxid of iron and alumina, filter, wash, ignite, and weigh as calcium oxid or titrate with potassium permanganate.

(e) Soluble Sulphate.

Boil 1 gram with 20 cc of strong hydrochloric acid, dilute to 200 cc with hot water, boil, filter, wash, and determine the sulphate in the filtrate by precipitation with barium chlorid in the usual manner. Calculate to calcium sulphate. If carbonates are present calculate the remaining calcium oxid to calcium carbonate (whiting); if carbonates are absent calculate the remainder as lime.

(f) Loss on Ignition.

Ignite 1 gram in a platinum crucible. The loss in weight represents water (both free and combined with gypsum and kaolin), carbon dioxid from whiting, and organic matter.

Barytes should contain only small amounts of foreign matter, and there should be 95 per cent or more of barium sulphate present.

5. Lithopone.

Lithopone should contain about 65 per cent of barium sulphate, the remainder being zinc sulphid with small amounts of zinc oxid and carbonate. This substance is also called ponolith and Beckton white.

(a) Analysis of Pure Lithopone (Drawe).

(1) Moisture.

Heat 2 grams of the sample for 2 hours at 105° C. There should be less than 0.4 per cent of moisture.

(2) Insoluble and Total Zinc.

Take 1 gram in a 200 cc beaker, add 10 cc of strong hydrochloric acid, mix, and add in small portions about a gram of potassium chlorate: then heat on the water bath until about half of the liquid is evaporated. Dilute with hot water, add 5 cc of dilute sulphuric acid (1:10), boil, allow to settle, filter, wash, ignite, and weigh the insoluble which will be total barium as barium sulphate, together with any other insoluble. Make a qualitative examination for alumina and silica (not likely to be present). Heat the filtrate from the insoluble to boiling, add sodium carbonate solution, drop by drop, until all of the zinc is precipitated as carbonate, filter on a gooch, wash, ignite, and weigh as zinc oxid.

(3) Zinc Sulphid.

Digest 1 gram with 100 cc of 1 per cent acetic acid at room temperature for one-half hour, then filter and wash: determine the zinc in the filtrate as in the preceding analysis. The difference between the total zinc oxid and the zinc oxid soluble in acetic acid multiplied by 1.1973 gives the zinc present as sulphid. The zinc soluble in acetic acid may be reported as oxid, though it may be partly carbonate. This scheme of analysis assumes the absence of impurities such as salts of iron, etc., and is the method of P. Drawe [a].

[a] Zts. angew. Chem., 1902, **15**: 174.

(b) Analysis of Lithopone in the Presence of Foreign Substances (Copalle).

Copalle[a] proposes the following method of analysis:

(1) Soluble Salts.

Wash 2 grams with hot water and determine the nature of the soluble salts.

(2) Moisture.

Determine on 2 grams the loss in weight on a steam bath.

(3) Insoluble.

Oxidize 1 gram with nitric acid of 40° B. (1.38 specific gravity), at first cold, then hot. Then add hydrochloric acid, evaporate to very small volume, dilute with hot water, filter, ignite the precipitate which represents the barium sulphate corresponding to the total barium. If the insoluble exceeds 66 to 68 per cent it is necessary to prove that the excess is not due to the addition of kaolin.

(4) Total Zinc.

Determine as oxid by precipitation as carbonate in the filtrate from the insoluble. When more than traces of iron, alumina, or lime are present, it is best to determine the zinc volumetrically.

(5) Sulphid of Zinc.

Add a slight excess of hydrochloric acid to the filtrate from the zinc carbonate and determine the sulphur by precipitation in the usual manner. This sulphur multiplied by 3.03, or the weight of barium sulphate ($BaSO_4$) multiplied by 0.4603, gives the zinc sulphid.

(6) Oxid of Zinc.

Multiply the weight of the zinc sulphid by 0.835 to obtain the zinc oxid corresponding to the sulphid. Subtract this from the total zinc oxid and report the remainder as zinc oxid (it may be present as oxid or as carbonate).

(7) Barium Carbonate.

Digest 2 grams with boiling dilute hydrochloric acid, dilute with hot water, filter from the insoluble and determine the barium in the filtrate by precipitation with sulphuric acid. The weight of the barium sulphate multiplied by 0.845 gives the barium soluble in the acid calculated as carbonate.

(8) Barium Sulphate.

Subtract the barium sulphate corresponding to the carbonate from the total barium sulphate.

6. General Scheme of Analysis for a White Pigment.

The pigment may contain white lead, lead sulphate, zinc oxid, baryta, whiting, kaolin, or other silicates, and, in fact, any mixture of white pigments, except lead compounds and zinc sulphid together, as such a mixture has a tendency to blacken.

---

[a] Ann. Chim. anal. appl., 1907, **12** : 62–65.

Dry 2 grams of the sample for 2 hours at 105° C. Treat 1 gram in a beaker with 25 cc of water and 10 cc of acetic acid (95 per cent) ; boil, filter, and wash with water. Pass hydrogen sulphid into the hot filtrate, collect the lead sulphid and zinc sulphid on a filter, wash, dissolve in nitric acid, precipitate, and weigh the lead as sulphate in the usual manner; calculate to white lead. In the filtrate from the lead sulphate determine the zinc either by the gravimetric or the volumetric method, and calculate to zinc oxid. Test the filtrate from the lead sulphid and the zinc sulphid for barium, calcium, and magnesium, determine in the usual manner, and calculate to carbonates. Transfer the residue from the acetic acid digestion to a beaker, add 10 cc of water, 10 cc of strong hydrochloric acid and 5 grams of ammonium chlorid, heat on a steam bath for 5 minutes, dilute with hot water to 400 cc, boil 5 minutes, filter, wash, ignite, and weigh the insoluble. Make a qualitative test of the insoluble. Precipitate the lead from the filtrate from the insoluble with hydrogen sulphid, dissolve in nitric acid, determine as sulphate, and calculate as lead sulphate. In the filtrate from the lead sulphid determine the alumina and the calcium in the usual manner; calculate the calcium found to calcium sulphate.

BLACK PIGMENTS.

Black pigments are practically all carbon black in one form or other. They should be tested for oil by washing with ether. Good quality black should be free from oil. Blacks which are alike chemically may behave very differently when ground in thin varnish. For example, lampblack mixed with such varnish in a ratio of 20 : 100 has flow, while gas-black similarly treated has no flow.

1. Manufactured Blacks.

(a) MOISTURE.

Dry 2 grams for 2 hours at 105° C. The loss in weight represents the moisture.

(b) VOLATILE MATTER.

Heat 1 gram in a well-covered platinum crucible for 7 minutes with a Bunsen flame 20 cm high. The crucible should weigh about 25 grams, have a well-fitting top, and be supported on a platinum triangle 7 cm above the top of the burner.

(c) ASH.

Ash 2 grams, preferably in a muffle, and weigh.

(d) SOLUBLE AND INSOLUBLE ASH.

Add to the ash from 2 grams of black 25 cc of hydrochloric acid (1 : 1), heat on a steam bath for 30 minutes, dilute with 75 cc of water, filter through a gooch, wash, ignite, and weigh the insoluble ash.

(e) ADULTERATIONS.

Blacks are occasionally adulterated with Prussian blue. To determine this point boil the sample with 4 per cent sodium hydroxid, filter, render the filtrate acid with hydrochloric acid and add a solution of a mixture of ferrous and ferric chlorid or sulphate. A blue precipitate indicates the presence of Prussian blue. At least one black on the market contains a large amount of a magnetic oxid of iron, which may be readily detected by the action of a magnet. The ash of ivory and bone blacks should contain a large amount of calcium phosphate.

2. Graphite.

Graphite is more of a gray pigment than a black. The finer grades are used as lubricants and in making lead pencils. All commercial graphite contains a considerable quantity of ash. For analysis, determine the moisture as usual, boil with hydrochloric acid, filter, dry and weigh, then ignite; it may be necessary to use oxygen to insure complete combustion; the loss is taken as carbon. If a previous test has shown the absence of carbonates, the treatment with hydrochloric acid may be omitted. Graphite used as a lubricant is sometimes adulterated with soft coal. Good Ceylon graphite is practically unaffected by hot sulphuric acid and potassium sulphate, while soft coal is completely decomposed. A fairly good quantitative determination of soft coal in graphite is made as follows:

Determine the moisture and the ash in one portion, and calculate the total carbon by difference. Treat 1 gram in a Kjeldahl digestion flask with 30 cc of strong sulphuric acid. Heat for two hours at a temperature about the fuming point of the sulphuric acid, cool, add water, filter, wash, dry, at 105° C., and weigh; then ignite until all of the carbon is burned; the loss here represents the carbon as graphite, and the difference between this determination and that of total carbon represents the soft coal.

COLORED PIGMENTS.

1. Yellow, Orange, and Red Pigments.

The most important yellow pigment is chrome yellow, which varies in shade from a light lemon yellow to a deep orange. The lighter shades generally contain lead sulphate as well as lead chromate, while the deep orange contains some basic lead chromate. Pure chrome yellow should contain only lead chromate, lead sulphate [a] and possibly some basic lead in the darker shades.

(a) CHROME YELLOW.

(1) MOISTURE.

Dry 2 grams for 2 hours at 105° C.

(2) INSOLUBLE IMPURITIES.

Treat 1 gram with 20 cc of strong hydrochloric acid, cover and heat on a steam bath for 15 minutes, add 100 cc of hot water, boil (the solution should be complete), filter, wash, ignite, and weigh the insoluble impurities.

(3) LEAD.

Evaporate the filtrate from the insoluble to about 2 cc, but not to dryness, add 100 cc of 95 per cent alcohol, stir, allow to stand for 1 hour, cool in ice water, filter on a Gooch crucible, wash with 95 per cent alcohol, dry for 1 hour at 110°C., cool, and weigh as lead chlorid. Multiply the weight of the lead chlorid by 0.74478 to obtain the amount of lead present.

(4) CHROMIUM.

Make the filtrate from the lead chlorid determination up to a definite volume, from an aliquot evaporate the alcohol, add water, then sodium peroxid in sufficient amount to render alkaline and to oxidize the chromium to chromate, boil

---

[a] Lead sulphate may be replaced by other insoluble lead compounds. A chrome yellow should be considered adulterated if it contains anything besides insoluble lead compounds.

until all of the hydrogen peroxid is driven off, cool, make acid with sulphuric acid, add a measured excess of standard ferrous sulphate and titrate the excess of iron with standard potassium dichromate.

(5) SULPHATE.

From another aliquot of the filtrate from the lead chlorid determination evaporate the alcohol, determine the sulphate in the ordinary way by precipitation and weigh as barium sulphate.[a]

(6) TREATMENT IN THE PRESENCE OF INSOLUBLE IMPURITIES.

If the sample contains no soluble impurities, the preceding method will give a complete analysis. When the qualitative test shows calcium it may be necessary to make the analysis in a somewhat different manner, for gypsum would by this treatment be precipitated with the lead chlorid and render the determination worthless. In such a case dissolve and separate the insoluble as above. Dilute the filtrate from the insoluble to 400 cc, cool, pass in a rapid stream of hydrogen sulphid until all of the lead is precipitated as lead sulphid, filter, wash with water containing some hydrogen sulphid, dissolve the lead sulphid in dilute nitric acid (hot), add an excess of sulphuric acid, heat to fumes and complete the determination of lead as sulphate in the usual way. In the presence of chromium the solution must be very dilute and the hydrogen sulphid passed in rapidly to get a good separation of lead as sulphid. Transfer the filtrate from the lead sulphid to a 500 cc flask, add ammonium hydroxid until it is slightly alkaline, pass in hydrogen sulphid until all of the zinc present is precipitated (in case no zinc is present the addition of hydrogen sulphid is unnecessary); make up to volume, mix, allow to settle, draw off aliquots of the clear liquid, and determine the calcium (and, if necessary, the magnesium) in the usual way. All the zinc and chromium will still be in the 500 cc flask; dissolve in hydrochloric acid, make up to the mark, mix, take out an aliquot and determine the zinc volumetrically by the ferrocyanid method as described under lead zinc whites. In another aliquot determine chromium as already described.

Sulphate can be determined by dissolving another portion in hydrochloric acid, filtering from it the insoluble, and precipitating with barium chlorid from the dilute hot filtrate; if the solution is kept dilute and hot, the barium sulphate precipitate will not be contaminated by lead.

(b) RED LEAD AND ORANGE MINERAL.

These pigments in the pure state are oxids of lead (approximately Pb_3O_4), being probably mixtures of compounds of varying proportions of lead monoxid and lead dioxid. Moisture, insoluble impurities, and total lead may be determined by the methods given under chrome yellow; or, in the absence of alkaline earth metals, the lead may be determined as sulphate in nitric acid solution (dissolve by adding a few drops of hydrogen dioxid) by evaporating with an excess of sulphuric acid until fumes of sulphuric anhydrid are evolved. Determine as sulphate in the usual way.

---

[a] Some chromes contain barium phosphate instead of lead sulphate, in which case test for phosphoric acid. Or barium sulphate, calcium sulphate, etc., may replace lead sulphate. Lead citrate is also sometimes present instead of lead sulphate.

The lead dioxid (PbO_2) may be determined as follows: Weigh 0.5 gram of the very finely ground pigment into a 150 cc Erlenmeyer flask. Mix in a small beaker 15 grams of crystallized sodium acetate, 1.2 grams of potassium iodid, 5 cc of water and 5 cc of 50 per cent acetic acid. Stir until all is liquid, pour into the Erlenmeyer flask containing the lead, and rub with a glass rod until all of the lead is dissolved; add 15 cc of water, and titrate with tenth-normal sodium thiosulphate using starch as indicator. A small amount of lead may escape solution at first, but when the titration is nearly complete this may be dissolved by stirring. The reagents should be mixed in the order given, and the titration should be carried out as soon as the lead is in solution, as otherwise there is danger of loss of iodin. One cubic centimeter of tenth-normal sodium thiosulphate corresponds to 0.011945 gram of lead dioxid.

These colored lead pigments may have their color modified by the addition of organic coloring matters. As a general rule, such adulteration may be detected by adding 20 cc of 95 per cent alcohol to 2 grams of the pigment, heating to a boil, and allowing to settle. Pour off the alcohol, boil with water, and allow to settle, then use very dilute ammonium hydroxid. If either the alcohol, water, or ammonium hydroxid is colored it indicates organic coloring matter. The quantitative determination of such adulteration is difficult and must generally be estimated by difference.

(c) VERMILION.

True vermilion, or, as it is generally called, English vermilion, is sulphid of mercury. On account of its cost it is rarely used in paints and is liable to gross adulteration. It should show no bleeding on boiling with alcohol and water and no free sulphur by extraction with carbon disulphid. A small quantity mixed with five or six times its weight of dry sodium carbonate and heated in a tube should show globules of mercury on the cooler portion of the tube. The best test for purity is the ash, which should be not more than one-half of 1 per cent. Make the determination in a porcelain dish or crucible, using 2 grams of the sample. Ash in a muffle or in a hood with a very good draft, as the mercury fumes are very poisonous. It is seldom necessary to make a determination of the mercury; but if this is required, it may be determined by mixing 0.2 gram of the vermilion with 0.1 gram of very fine iron filings, or better " iron by hydrogen." Mix in a porcelain crucible and cover with a layer 10 mm thick of the iron filings, place the crucible in a hole in an asbestos sheet so that it goes about half way through, cover with a weighed, well fitting, gold lid which is hollow at the top, fill this cavity with water, heat the crucible for 15 minutes with a small flame, keep the cover filled with water, cool, remove the cover, dry for 3 minutes at 100° C., and 30 minutes in a desiccator, and weigh. The increase in weight is due to mercury. The mercury can be driven off from the gold by heating to about 450° C. A silver lid may be used, but gold is much better.

Another method is to place in the closed end of a combustion tube 45 cm long and 10 to 15 mm in diameter a layer of 25 to 50 mm of roughly pulverized magnesite, then a mixture of 10 to 15 grams of the vermilion with four or five times its weight of lime, followed by 5 cm of lime, and plug the tube with asbestos. Draw out the end of the tube and bend it over at an angle of about 60°. Tap the tube so as to make a channel along the top, and place it in a combustion furnace with the bent neck down, resting with its end a little below some water in a small flask or beaker. Heat first the lime layer, and carry the heat back to the mixture of lime and pigment. When all the mer-

cury has been driven off, heat the magnesite, and the evolved carbon dioxid will drive out the last of the mercury vapors. Collect the mercury in a globule, wash, dry, and weigh.

Genuine vermilion is at the present time little used in paints. Organic lakes are used for most of the brilliant red, scarlet, and vermilion shades. These organic coloring matters are sometimes precipitated on red lead, orange mineral, or zinc oxid; but as a usual thing the base is barytes, whiting, or china clay. Paranitranilin red, a compound of diazotized paranitranilin and beta-naphthol is largely employed; but a number of colors may be used. To test for red colors in such a lake the following method from Hall [a] may be of value, though other colors may be employed, which makes the table of only limited use.

Determination of red colors in organic lake.

Reagent.	Source of color.				
	Alizarin.	Eosin.	Para-nitrani-lin.	Ortho-anisi-din.	Scarlet (2R).
Sulphuric acid, conc.	Dark brown with reddish under-tone becoming light yellow on diluting.	Changes to yel-low; fluores-cent solution with excess of sodium hy-droxid.	Purple; color returning on diluting.	Purple; red on diluting.	Darkened; lighter on diluting.
Hydrochloric acid, conc.	Color becomes "muddy."	Changes to yel-low; reddish fluorescent solution with excess of so-dium hydrox-id.	Color slightly darkened; lighter on diluting.	Dark purplish red; lighter on diluting.	Darkened; lighter on diluting.
Sodium hy-droxid, conc. sol.	Dark reddish brown; little change on di-luting.	Little change; fluorescent solution on diluting.	Color changed to brownish red; light red on dilut-ing.	Little change.	Reddish solu-tion on di-luting.
Alcohol	Insoluble.........	Reddish fluo-rescent solu-tion.	Slight yellow-ish, orange solution.	....	Slight reddish solution.
Sodium hy-droxid, conc. and al-cohol.	Purplish; dark brown on dilut-ing.	....	Purple; color returning on diluting.	Little change.	Color darker; reddish solu-tion on di-luting.

It is well also to try the action of reducing and oxidizing agents such as stannous chlorid, ferric chlorid, etc. (See also Schultz and Julius, A System-atic Survey of the Organic Coloring Matters.)

Paranitranilin red is soluble in chloroform. It is also well to try the solvent action on different reds of sodium carbonate, etc. The amount of organic pig-ment present in such reds is generally very small, and when it can not be determined by ignition owing to the presence of lead, zinc, or carbonate, it is best determined by difference.

2. Oxid and Earth Pigments.

Iron oxid is extensively used as a paint. The native oxid naturally varies very much in its composition. In general, however, only the poorer grades of native hematite are used as paints. Artificial iron oxid pigments, made by calcining copperas may be practically pure ferric oxid. Umbers, ochers, and siennas are earthy substances containing iron and manganese oxids and more or less organic matter.

[a] The Chemistry of Paints and Paint Vehicles, p. 29.

The methods of analysis are very much the same as those for iron ores. It is generally sufficient to determine moisture, loss on ignition, insoluble in hydrochloric acid, ferric oxid, and manganese dioxid. If much organic matter is present, roast 2.5 grams in a porcelain dish at a low temperature until all organic matter is destroyed, add 25 cc of hydrochloric acid, cover with a watch glass and heat on the steam bath for two hours; then add 10 cc of sulphuric acid (1 : 1), evaporate, and heat until fumes of sulphur trioxid are evolved and all the hydrochloric acid is driven off. Cool, add 50 cc of water, boil until all of the iron sulphate is dissolved, filter into 250 cc graduated flask, fill to the mark, mix, and take out a portion of 50 cc for iron determinations. For the determination of iron reduce with zinc, titrate with standard potassium permanganate, and calculate to ferric oxid. For the determination of manganese transfer 100 cc of the solution (corresponding to 1 gram) to a 500 cc flask, add sodium hydroxid solution until nearly but not quite neutral. Then add an emulsion of zinc oxid in water in slight excess, shake until all of the iron is thrown down, fill to the mark, mix, let settle, filter through a dry paper, and use portions of 100 cc (corresponding to 0.2 gram) for the manganese determination. Transfer to a 300 cc Erlenmeyer flask, heat to boiling, titrate with standard permanganate. The flask must be shaken during the titration and some experience is necessary to determine the end point, which is best seen by looking through the upper layer of liquid and observing when the pink tinge from the permanganate does not disappear on shaking. A standard potassium permanganate solution, the iron factor of which is known, may be used to determine manganese. The iron factor multiplied by 0.2952 gives the manganese factor. In some cases this method of attack will not separate all of the iron from the insoluble matter. In such a case the insoluble must be fused with a mixture of sodium and potassium carbonates, dissolved in water, evaporated with excess of sulphuric acid, filtered from the insoluble, and this solution added to the first one.

Another method is as follows: Roast 5 grams of the powder, digest with 25 cc of hydrochloric acid, evaporate to dryness, moisten with hydrochloric acid, dissolve in water, filter, and wash the residue; ignite the residue in a platinum crucible, add sulphuric acid and hydrofluoric acid, drive off the latter, and heat until copious fumes of sulphuric anhydrid come off. Add potassium hydrogen sulphate and fuse, dissolve in water, filter from any remaining insoluble (barium sulphate), unite the two solutions, make up to 500 cc, and use aliquots for the iron and manganese determinations. For the determination of iron place 100 cc in a flask, add about 3 grams of zinc, put a funnel into the neck of the flask, heat when the action slackens; if basic salts separate out add a few drops of hydrochloric acid. When all of the iron is reduced add 30 cc of sulphuric acid (1 : 2) and as soon as all of the zinc is dissolved and the solution is cool, titrate with potassium permanganate.

For the determination of manganese use 50 cc, evaporate to a very small bulk, add strong nitric acid and evaporate the hydrochloric acid; add 75 cc of strong nitric acid, which should be free from nitrous acid, and 5 grams of potassium chlorate, heat to boiling and boil 15 minutes; then add 50 cc of nitric acid and more potassium chlorate. Boil until yellow fumes cease to come off, cool in ice water, filter on asbestos and wash with colorless, strong nitric acid; suck dry and wash out the remaining nitric acid with water, transfer the precipitate and the asbestos to a beaker, add a measured excess of standard solution of ferrous sulphate in dilute sulphuric acid, stir until all of the manganese dioxid is dissolved, and titrate the remaining ferrous sulphate with potassium permanganate. A ferrous solution of about the proper strength is made by dissolving 10 grams of crystallized ferrous sulphate in 900 cc of

water and 100 cc of sulphuric acid (specific gravity 1.84). This solution is titrated with standard potassium permanganate. The reaction taking place when the manganese dioxid acts on the ferrous sulphate is $MnO_2+2FeSO_4+2H_2SO_4=MnSO_4+Fe_2(SO_4)_3+H_2O$. Hence the iron value of permanganate multiplied by 0.491 gives the value in manganese.

3. Blue Pigments.

There are two important blue pigments used in painting, Prussian blue and ultramarine. Of minor importance and very little used in paints for anything but artists' colors are cobalt blue and smalt.

(a) PRUSSIAN BLUE.

Under the name Prussian blue are included all ferrocyanid blues such as Antwerp blue, Chinese blue, Turnbull's blue, etc. These blues are all ferric ferrocyanids, ferrous ferricyanids, or double iron potassium salts of hydroferrocyanic or hydroferricyanic acids. The analysis of these blues, as is generally the case with pigments, does not necessarily give results which can be used to grade samples, the strength and color tests being most important. Most text books say that Prussian blue is ferric ferrocyanid, $Fe_4[Fe(CN)_6]_3$, but this substance is not known commercially. Commercial Prussian blue is a mixture of Williamson's blue, $KFe[Fe(CN)_6]$, with other iron-alkali cyanids and often with aluminum-iron cyanids, altogether a most complex substance.[a]

(1) MOISTURE.

For the determination of moisture dry 2 grams for two hours at 100° C. Dry blue should contain less than 7 per cent of moisture.

(2) INSOLUBLE IMPURITIES.

Ignite 1 gram in a porcelain dish at a low temperature. The ignition should be carefully carried out at a temperature just high enough to decompose the last trace of blue, but not high enough to render the iron insoluble, or very difficultly soluble in hydrochloric acid. Cool, add 15 cc of hydrochloric acid, digest for an hour on the steam bath covered with a watch glass, evaporate to a sirup, add water, boil, filter from the insoluble, wash, ignite, weigh, and determine the nature of the insoluble, probably barium sulphate. In pure Prussian blue solution should be complete.

(3) TOTAL IRON.

Decompose as in the foregoing determination, reduce, and determine the iron in the ordinary way. There should not be less than 30 per cent, calculated on the dry pigment.

(4) TOTAL NITROGEN.

Determine on a 1 gram sample by the official Gunning method, digesting for three hours.[b] The percentage of Prussian blue may be obtained with sufficient accuracy for commercial purposes by multiplying the percentage of nitrogen by 4.4 and by multiplying the percentage of iron by 3.03. Eight samples

---

[a] Parry and Coste, The Analyst, 1906, **21**: 225-230.
[b] U. S. Dept. Agr., Bureau of Chemistry, Bul. 107, p. 7.

of pure Prussian blue examined by Parry and Coste gave the mean results from which these factors are calculated. The following table shows the accuracy with which these factors give the percentage of Prussian blue in the eight samples:

Parry and Coste's determination of the percentage of Prussian blue in the dry matter of eight samples.

Factors.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.
Nitrogen × 4.4	94.69	100.93	107.58	94.91	98.95	99.83	100.80	102.52
Iron × 3.03	94.63	101.02	109.71	97.11	94.84	98.99	102.47	100.26

(5) OTHER DETERMINATIONS.

It is seldom worth while to make any further determinations. If desired, however, the iron and aluminum may be precipitated as hydrates by ammonium hydroxid and weighed together as oxids, and the aluminum obtained by difference after determining the iron volumetrically and calculating to ferric oxid. The filtrate from the iron oxid and alumina precipitate may be made up to a definite volume and one aliquot taken for the determination of sulphate and another evaporated with sulphuric acid, ignited, and weighed. Determine whether the alkali is sodium or potassium and subtract the alkali metal corresponding to the sulphate (SO_4) found. The remainder is double alkali iron ferrocyanid. Well-washed blues should be neutral in reaction. The red shade may be due to organic red. Test the solubility in alcohol, etc.

(b) ULTRAMARINE.

Ultramarine is a compound of unknown constitution made by heating clay, soda, sulphur, and charcoal together. It appears to be complex silicate and sulphid of aluminum and sodium. Ultramarine may be readily distinguished from Prussian blue by being dissolved in hydrochloric acid with the evolution of hydrogen sulphid. It can not be mixed with lead pigments on account of the sulphid present. Good ultramarine gives little tarnish on polished copper. An analysis is of little value, but if desired may be conducted as follows:

(1) MOISTURE.

Dry 2 grams for 2 hours at 105° C.

(2) SILICA.

Treat 1 gram with 20 cc of hydrochloric acid (1 : 1) in a covered dish, heat until decomposed, remove the cover and evaporate to dryness on a water bath, moisten with hydrochloric acid and again heat to dryness, add 1 cc of hydrochloric acid, let stand 5 minutes, add hot water, filter, and wash the insoluble. If great accuracy is desired, evaporate the filtrate to dryness, take up with hydrochloric acid and water, filter, and add the precipitate to the main insoluble. Ignite the insoluble, weigh as silicon dioxid, and test the purity with hydrofluoric acid.

(3) ALUMINUM.

Determine the aluminum in the filtrate from the silicon dioxid by precipitating with ammonium hydroxid, igniting, and weighing as aluminum oxid.

(4) SODA.

Add sulphuric acid to the filtrate from aluminum hydroxid, evaporate to dryness, ignite, and weigh as sodium sulphate (Na_2SO_4). Calculate to sodium monoxid (Na_2O). If calcium is present it should be precipitated with ammonium oxalate in the filtrate from aluminum hydroxid, ignited, and weighed as calcium oxid and the soda determined in the filtrate from the calcium oxalate as described previously.

(5) SULPHUR.

Mix 1 gram of ultramarine with 4 grams of sodium carbonate and 4 grams of sodium peroxid in a nickel crucible, cover with about a gram of sodium carbonate, fuse, using an aluminum or asbestos shield to prevent the sulphur from being taken up from the gas. Dissolve the fusion in water, making acid with hydrochloric acid; there is no insoluble residue. Precipitate with barium chlorid and determine total sulphur by weighing the barium sulphate.

(6) SULPHUR AS SULPHATE.

Weigh 1 gram in a beaker, add water, then hydrochloric acid, boil until the hydrogen sulphid is expelled, then add barium chlorid, and determine the sulphur as usual by weighing the barium sulphate.

(7) SULPHUR AS SULPHID.

Subtract sulphur as sulphate from the total sulphur. Pure ultramarine will generally have about the following composition :

	Per cent.
Silicon dioxid (SiO_2)	39 to 43
Alumina (Al_2O_3)	24 to 30
Sodium monoxid (Na_2O)	17 to 21
Sulphur (S)	10 to 16

4. Chrome Green.

The most important green pigment is chrome green, which is a mixture of Prussian blue and lead chromate. Where absolute permanence is required chromium oxid (Cr_2O_3) is sometimes used, but this pigment is not common. The very brilliant copper arsenic compounds (Paris green, etc.) are little used in paints.[a]

(a) GENERAL DISCUSSION.

A pure chrome green should contain only Prussian blue, lead chromate, and lead sulphate. Any other substances should be considered adulterants. Greens made by precipitating the ingredients together are superior to those made by mixing the blue and yellow after they are precipitated separately. To distinguish the two, rub up the pigment in oil and allow to stand. A badly made green will show blue, but one properly made by precipitation will not. A microscopic examination of the dry pigment should also be made. A badly made green will show yellow and blue particles, as well as green. A well made green will show green and some blue particles, but no yellow.

As different grades of lead chromate vary greatly in shade, and as the same is true to a somewhat less extent with Prussian blue, actual determinations of the percentages of Prussian blue, lead chromate, and lead sulphate are of little real

---

[a] For methods of analysis see U. S. Dept. Agr., Bureau of Chemistry, Bul. 107, pp. 25–30 ; also, Lunge, Chemisch-technische Untersuchungs Methoden, **2** : 807–810.

value, and the analysis of chrome green is made with difficulty. It is, however, important to determine impurities, which may be barium sulphate, silica and silicates (clay), or calcium and magnesium compounds.

(b) Impurities.

To examine for impurities proceed as follows: Place 1 gram in a small casserole, add 10 cc of water and sodium peroxid, a little at a time (about 1 gram in all), to oxidize the Prussian blue; add about 25 cc more of water and boil for some time, so as to decompose all of the hydrogen peroxide. Acidify with hydrochloric acid, boil, filter, and wash. Transfer the residue again to the casserole and boil with a solution of ammonium chlorid (slightly alkaline) to dissolve the last trace of lead; filter, wash, ignite, weigh the insoluble impurities, and determine their nature. They are probably barytes or silica.

Heat another 1 gram portion very gently in a casserole or small porcelain dish, and remove from the flame as soon as it begins to glow. The heating should be carried out very carefully, the object being to decompose the Prussian blue, but not to heat it enough to render the iron difficultly soluble. Allow to cool, add hydrochloric acid, and digest covered on the steam bath for an hour. As a general rule, this treatment brings everything except insoluble impurities into solution. Cool, dilute to 300 cc and pass in a rapid stream of hydrogen sulphid until all of the lead is precipitated; filter, wash with water containing some hydrogen sulphid, boil off the hydrogen sulphid from the filtrate, add bromin water to oxidize the iron, add ammonium hydroxid in slight excess, filter, dissolve the precipitate in hydrochloric acid, reprecipitate with ammonium hydroxid, filter, wash, unite the filtrates, and determine calcium and magnesium in the usual way.

(c) Quantitative Determination of Yellow and Blue.

The examination for impurities is usually sufficient, but if a quantitative determination of yellow and blue be desired, the sulphate may be determined in the united filtrate from the insoluble impurities by precipitating from hydrochloric acid with barium chlorid. The ferric ferricyanid present will not cause any difficulty if the barium sulphate is filtered off soon after precipitating; but if it is allowed to stand a long time a reduction is likely to take place with the re-formation of some Prussian blue.

Determine the lead in the second portion by dissolving the lead sulphid in nitric acid, boiling the residues with ammonium acetate, uniting the filtrates, adding sulphuric acid, heating to fumes, and completing the determination of lead as sulphate in the usual manner. For iron and chromium dissolve the ammonia precipitate in hydrochloric acid, make up to definite volume, determine the iron in an aliquot by reduction and titration with potassium permanganate or potassium dichromate. Determine the chromium in another aliquot as described under chrome yellow.

(d) Miscellaneous Determinations.

If aluminum is present, precipitate another aliquot with ammonium hydroxid, wash, dry, ignite, and weigh. From the iron and chromium determinations calculate the combined weight of ferric oxid and chromium oxid and obtain aluminum oxid by difference. Determine the moisture and the nitrogen as described under Prussian blue.

If the presence of ultramarine is suspected, test with hydrochloric acid, and if hydrogen sulphid is evolved, ultramarine is present.

MIXED PAINTS.

Single pigments are generally sold either dry or ground in oil alone; rarely do they contain thinners or driers. Ready-mixed paints, however, contain, in addition to oil, turpentine or gasoline and usually some drier. More complicated yet are enamel paints which are pigments ground in oil varnish, and contain, beside the substances in the vehicle of mixed paints, varnish gums.

The can of mixed paint should not be shaken, but should be weighed as a whole, opened, and as much of the clear vehicle removed as possible; this should be weighed and kept in a stoppered flask (use cork, not rubber stopper). After removing the clear vehicle mix the contents of the can thoroughly and transfer to another jar. Wipe and weigh the can. These figures will give the necessary data for calculating the analytical results back to the original material.

1. Extraction of the Vehicle.

Weigh from 15 to 35 grams of the thoroughly mixed pigment in a tall, narrow Erlenmeyer flask of 300 cc capacity. Add 150 cc of gasoline, stopper with a cork, and shake for 10 minutes with a shaking machine so constructed that the liquid is not brought in contact with the stopper; allow to stand until the pigment has settled, and decant the liquid into a beaker; some pigment will frequently go over with the gasoline, so it is well to allow this to settle and decant into a second beaker. Repeat the treatment with gasoline; after the first treatment settling is generally much more rapid. Decant the gasoline as completely as possible the second time. Then add 150 cc of benzol (C_6H_6), shake, and allow to settle. Decant the benzol and treat in same way with 150 cc of ether. This method of extraction is often more satisfactory than any method using a continuous extraction apparatus; for frequently the pigments can not be held by extraction thimbles. This method of treatment will generally give an almost complete separation of the vehicle; but in some enamel paints it is well to follow the gasoline treatment by a treatment with turpentine, and then remove the turpentine with gasoline, before treating with benzol and ether. No system of extraction will remove absolutely all the vehicle, the insoluble portion being probably metallic soaps or linoxyn.

After removing all of the soluble vehicle, dry the pigment, first at a low temperature in a gentle current of air, and then at 105° C.; weigh, and from the loss in weight calculate the percentage of vehicle and pigment; then from the total weight of mixed paint and the weight of clear vehicle drawn off calculate the percentage of vehicle and pigment in the original paint.

2. Analysis of Pigment.

Follow the methods for dry colors. In general determine the amount insoluble in hydrochloric acid and the nature of the insoluble, and make an analysis of the soluble portion. In the absence of carbon and hydrated silicates (clay, etc.), a fairly close determination of unextracted vehicle may be made by drying the insoluble at 105° C., weighing, and then igniting and weighing. This loss is called combined water and carbonaceous matter, and in many cases may be safely considered as unextracted vehicle.

3. Analysis of Vehicle.

Weigh 50 grams of the vehicle into a 500 cc flask, connect with a spray trap and a vertical condenser, and pass through it a current of steam, first heating the flask in an oil bath at 100° C.; with the steam still passing through,

raise the temperature of the bath to 130°. Catch the distillate in a small weighed separatory funnel; continue distillation until the funnel contains 150 cc of water. Let the distillate stand until separated into two layers, then draw off the water, and weigh the light oils. Examine as under turpentine, page 8.

A slight error is caused by the solubility of turpentine in water; this amounts to about 0.3 to 0.4 cc for each 100 cc of water. Cut off the steam, remove the trap, and draw air through the flask for about 15 minutes, keeping the oil bath at 130° C. The residue is now free from water and can be examined according to the following procedure for the residue from dry distillation.

When sufficient vehicle is available it is well to take another portion and distil, without steam, placing the flask in an air bath. Note the temperature of the bath at which distillation takes place, and continue the distillation at a tempertaure of 185° C. in the air bath. This method gives somewhat lower results on volatile oils than the first method, but the distillate can be tested for water-soluble volatile liquids which would be lost by the steam distillation. Unsaponifiable matter should be determined in this residue, or in some of the original vehicle. (See examination of linseed oil, page 7.)

The residue is frequently too pasty for the determination of the specific gravity, which should be made on the original vehicle. Determine the acid number of the residue and of the original vehicle. Determine the percentage and the character of the ash either from the residue or the original vehicle. The iodin number is sometimes a useful index; but the constants of linseed oil which has been mixed with pigments, especially lead compounds, may be so much altered that an iodin number as low as 100 can not be taken as any proof of the presence of other fatty oils.

Test for rosin as described under linseed oil. Another test for rosin may be made by dissolving in carbon disulphid and adding a solution of stannic bromid or chlorid in carbon disulphid. Use a white porcelain dish. If no water is present in either solution the presence of rosin is shown by the appearance of a violet color. This test is not as delicate as the Liebermann-Storch test described under linseed oil.

When much lead is present it may be lost in ashing, and for a correct determination of metals the following method is best: Place 25 grams of the vehicle in a 500 cc separatory funnel, dilute with 25 cc of a mixture of equal parts of gasoline and turpentine, add 50 cc of nitric acid (1 : 1), and let stand one hour, shaking every ten minutes. Then immerse the funnel in hot water, loosen the stopper and shake gently. This drives off nearly all the gasoline. Remove from the hot water, let it separate, draw off the lower layer, and wash the upper oily layer four or five times with warm water. Add the washings to the main acid portion and determine the metals in the ordinary manner. If the paint is enamel paint, treat the vehicle as a varnish. (See page 9.)

INKS.

WRITING INKS.

Almost without exception all black inks suitable for record purposes are iron-tannin inks. The determinations of an analytical character which are of value are as follows:

1. Specific Gravity.

Determine with a pyknometer at 15.6° C.

2. Total Solids.

Weigh 10 grams of ink in a flat-bottomed platinum or porcelain dish, evaporate to dryness on the water bath, and then heat in an oven at the temperature of boiling water for 2 hours; cool in a desiccator and weigh.

3. Ash.

Burn the residue from the determination of total solids at a low temperature, preferably in a muffle. In order to avoid loss by foaming the dish used should not be too small, not less than 50 cc capacity.

4. Iron.

Transfer the ash to a small beaker and dissolve in 15 cc of hydrochloric acid with the addition of stannous chlorid at the temperature of the steam bath; reduce by adding stannous chlorid, drop.by drop, to the hot solution until the color is destroyed, and then add one or two drops in excess. Wash the reduced iron solution from the small beaker into a 600 cc beaker and dilute to about 250 cc with cold water, add all at once an excess of mercuric chlorid, stir. allow to stand a minute, and titrate with standard potassium dichromate solution.

5. Sulphuric Anhydrid (SO_3.)

Determine both iron and sulphuric anhydrid in the same sample. Place from 10 to 15 grams of ink in a platinum dish, add 1 to 1.5 grams of sodium carbonate previously dissolved in water, evaporate to dryness, ash, extract with water, add bromin water to the extract, boil, render acid with hydrochloric acid, boil off the bromin, and determine the sulphuric anhydrid (SO_3) by precipitation with barium chlorid. Dissolve the insoluble residue in hydrochloric acid and determine iron as described in the preceding section. Or, in case the small amount of platinum (which always goes into solution when iron oxid is dissolved by hydrochloric acid in platinum) causes trouble with the potassium dichromate method, add sulphuric acid, evaporate to fumes, dilute, reduce with zinc, and titrate with potassium permanganate.

6. Exposure Tests.

For exposure tests see Schluttig and Neumann,[a] Mitchell and Hepworth,[b] and Munson.[c] The chromate logwood inks and the vanadium inks are not permanent. Among the inks examined by Munson no sample with a specific gravity below 1.035 was permanent, and with one exception, no sample containing less than 0.60 per cent of iron. The exception, however, was a very permanent ink, in spite of the fact that it contained only 0.32 per cent of iron.

CANCELING INKS HAVING AN OIL BASE.[d]

The following methods have been devised for the purpose of ascertaining the suitability of canceling inks for the use of the Post-Office Department. Many of these methods will be found of assistance in passing upon the quality of stamping inks for miscellaneous uses.

---

[a] Die Eisengallustinten.

[b] Inks, Composition and Manufacture.

[c] The Examination of Writing Inks, J. Amer. Chem. Soc., 1906, **28**: 512.

[d] The work on canceling inks is a revision of the methods previously issued as Circular 12 of this Bureau.

It is important that the ink used by the Post-Office Department for post-marking possess in the highest possible degree certain properties. The ink, first of all, must produce an indelible cancellation; that is, it must be relatively indelible as compared with the ink used for printing the postage stamps. The postmark made with the ink must dry quickly in order that the mail matter may be handled immediately without any blurring or smearing of the post-mark. Both this property and the property of indelibility involve the question of the rate at which the ink penetrates or is absorbed by the fiber of the paper. A satisfactory ink does not harden or form a crust on the ink pad on exposure to the air. There must be no deposition of solid matter on the bottom of the vessel in which the ink is stored, and the pigments, on which the indelibility of the ink depends, if insoluble, must not settle out in such a way as to make it possible to pour off from the top of the container a portion of the ink which contains little or none of the insoluble pigment or pigments. The following methods have been found of value for the purpose of ascertaining the quality of a given sample of ink as well as the appropriateness of certain materials used for the manufacture of canceling inks.

1. Preparation and Care of the Sample.

Since canceling inks contain more or less insoluble and volatile matter, special attention must be given to the preparation and care of the sample. It must be carefully mixed by shaking before each portion is removed for analysis, and the container must be left open no more than is absolutely necessary for the removal of portions of the ink.

2. Determination of Matter Volatile at Ordinary Temperatures.

Place a carefully weighed quantity (between 5 and 5.2 grams) of the ink in a flat-bottomed aluminum dish 102 mm (4 inches) in diameter. Distribute the ink completely over the surface of the bottom of the dish by gently tilting the same. This quantity of ink should be sufficient to completely cover the bottom of the dish. Place the dish on a horizontal shelf or table where air will have free access to it and where it will be screened in such a way that no dust can fall into it.

Reweigh the dish at the end of 18 hours, 24 hours, 2 days, 3 days, 4 days, 5 days, 6 days, 7 days, 14 days, 21 days, and 28 days. Calculate the total per-centage loss of weight at the end of each period of drying. The loss of weight should be gradual and should not exceed 15 per cent during the first 7 days, nor 25 per cent during 28 days. This test shows the absence of highly volatile in-gredients and the absence of an excess of matter volatile at the ordinary room temperature. The constituents of a canceling ink should be such that the vola-tile matter will not exceed the above limits when the ink is exposed under the conditions named to a summer temperature of 80° F. and upward.

3. Determination of Relative Penetrating Power.

(a) APPARATUS.

(a) Homeopathic shell vials about 8 cm long and 2 to 2.5 cm in diameter.

(b) Strips of white blotting paper, which for a given series of determinations should be cut from the same sheet and of exactly the same dimensions. A con-venient size is 12 mm wide and 25 cm long.

(c) A pair of dividers with arms 15 cm long or longer.

(d) A millimeter rule.

(b) Determination.

Place approximately 5 cc of the ink or other material to be tested in one of the " shell vials " described, and if several samples are to be tested arrange the vials in a row. Place 5 cc portions of distilled water in each of two of the vials, and put one of the vials containing water at each end of the row of vials containing samples to be tested. Proceeding from left to right, insert a strip of blotting paper in each of the vials, recording the exact time the paper was placed in each vial. The blotting paper should maintain a nearly upright position. The liquids gradually ascend the strips by capillarity; the strips, however, should be in such a position that the liquid does not ascend by capillarity between the edges of the strips and the sides of the vials.

At the expiration of exactly 15 minutes from the time each strip is inserted in the vial, measure the height to which the liquid has ascended the strip of paper by means of a pair of dividers and record the distance in millimeters. Make a second set of readings at the end of 45 minutes.

After all of the measurements have been recorded reduce the results to the terms of the penetrating power of distilled water, taking the penetrating power of distilled water as 100. This is accomplished by dividing each result by the average of the results obtained for the distilled water contained in the vials and multiplying the quotient by 100. Ten samples may conveniently be tested at one time by working as described. The method gives good comparative results, and has been applied not only to canceling and other stamping inks, but to the liquids used for the manufacture of these inks.

In observing the penetrating power of a given sample of ink it is important to remember that the value of a canceling or stamping ink depends upon its power to penetrate the paper during the first minute or fraction of a minute following its application to the paper. It is well, however, to keep the tests under observation for several hours, as information can thus be obtained in regard to the extent to which the coloring matter contained in the ink follows the liquid base of the ink as it passes through the paper. In some cases the coloring matters keep pace with the liquid portions of the ink; in others an uncolored band at the top of the portion of the paper which is wet with the ink shows that the coloring matter does not proceed through the paper as rapidly as the base of the ink. This may or may not be an undesirable result. If the colorless band is due to a difference in the rate of penetration, it is undesirable. If it shows that the dye contained in the ink has an affinity for the fibers of the paper, it is evidence of a valuable quality.

Additional information can be obtained from the penetration test by removing the strips of paper from the vials, cutting off the part of the paper which has actually been immersed in the ink, and treating the upper part successively with petroleum, ether, alcohol, and other solvents for removal of the constituents of the ink soluble in these liquids. The extent to which the dye or dyes contained in the ink resist the action of these solvents and the extent to which the lampblack has passed up the strip of blotting paper are indices of the quality of the ink.

An examination of the strips with the microscope will give valuable information regarding the rise of carbon in the paper and the affinity of the dye for the fibers of the paper. With many inks the carbon will not rise above the surface of the liquid, while with others it penetrates the paper to the same height as the dye. With this class of inks it is important that the base of the ink have the power to carry the carbon well into the fibers of the paper.

To make the determination allow the strips to remain in position until the next day, remove, dry between blotters, and examine for a rise of dye or carbon.

If either dye or carbon rises as far, or nearly as far, as the base of the ink the rise is pronounced " satisfactory." Less than this is not acceptable except in the case of glycerin inks, which rarely give any rise of carbon. A small amount of rise in the latter inks must be accepted as satisfactory. To determine whether the rise is carbon or simply dye, pick off particles of the paper and adhering ink at intervals on the strip and mount on slides with water or alcohol. Examine with the microscope, using low power; note size of the carbon grains. The grains adhere to the outside of the paper fibers in clots, as a rule. It is often difficult to distinguish the carbon grains.

4. Sedimentation Test.

(a) APPARATUS.

(1) Glass-stoppered cylinders, graduated for 200 cc and fractions thereof, the distance between the bottom and the 200 cc mark being 25 cm (10 inches). If unobtainable, other cylinders may be substituted, marks being placed at distances 25 cm (10 inches) and 16 mm ($\frac{10}{16}$ inch) from the bottom.

(2) A pair of dividers with arms 15 cm long or longer.

(3) A millimeter rule.

(4) Pipettes made from straight tubing (7 mm), at least 30 cm in length and having a capacity of from 10 to 15 cc.

(b) DETERMINATION.

By means of the special pipette introduce carefully, drop by drop, into one of the 200 cc cylinders, exactly 16 mm depth of the ink to be tested. The ink should be previously tested to determine a proper solvent for both base and dye. Alcohol is generally the solvent to use for rosin inks. It may be necessary to use other solvents, such as gasoline (boiling point 50° to 60° C.), ether, benzol, etc. Dissolve the ink in the cylinder in the appropriate solvent and dilute up to the 200 cc mark, stopper, and shake thoroughly. Allow the cylinder to stand, and record from time to time, by using the dividers and millimeter rule, the height of the top of the layer of sediment which collects in the bottom of the cylinder, expressing results in millimeters. During the first hour observations should be made at intervals of 15 minutes; later, each hour for several hours successively, and then twice daily for a week to ten days.

After the settling of the top of the layer of sediment has entirely ceased, the height of the sediment should equal or exceed 16 mm, the amount of ink taken for the test. The rate of sedimentation is an index of the state of division of the carbon, some inks showing no appreciable layer at the expiration of a ten-day test.

In the case of some inks the supernatant liquid above the sediment is of such a dark color that there is difficulty in locating the top of the sediment, even when the cylinder is inspected by light reflected at various angles. In this event, the use of a dark room with a light placed so as to give a strong ray through a small aperture will locate the top of the layer of sediment in all cases except when the ink contains a very large percentage of a dense dye.

Frequently the layer may be located by holding an incandescent electric light back of the cylinder and noting where the carbon filament can not be seen. The test is somewhat crude and only approximate, but it serves to give an idea of the fineness and amount of carbon, and, as a rule, agrees fairly well with the carbon determinations.

5. Determination of Lampblack.

Load a porcelain gooch with asbestos, using a felt about one-fourth of an inch thick. After washing the felt thoroughly with water to remove fine particles, finally wash with alcohol and ether, dry, and weigh. Weigh out about 5 grams of ink in a small beaker, dilute with a suitable solvent (alcohol is used in case of rosin-oil inks), transfer to a Gooch crucible, and wash until all oil and soluble color is removed. Finally, wash with alcohol and ether, dry, and weigh.

6. Determination of Ash.

The lampblacks prepared for the manufacture of canceling ink yield less than 0.5 per cent of ash when burned, and the coal-tar dyes employed should contain no mineral matter other than that which is an essential part of the molecules of the substances to which the tinctorial power of these dyes is due.

For the determination of the ash, place 2 to 3 grams of the ink in a porcelain dish, which must be of such size as to avoid loss of ink due to the foaming which is likely to attend the beginning of the incineration. Heat the dishes thus charged in a muffle at a low red heat, until all organic matter and uncombined carbon have been burned. Cool and weigh.

If an excessive percentage of ash is found, the percentage of mineral matter contained in the alcoholic extract should be determined by incineration of the residue obtained after evaporation of this extract. If either the total ash or the ash of the alcoholic extract is high, a qualitative examination should be made.

7. Resistance of Pigments and Dyes to Light and Reagents.

It is necessary in the case of canceling inks, and important, if not necessary, in the case of many stamping inks, that the pigments and dyes employed in their manufacture be as resistant as possible to means which may be employed for the erasure of marks made by them on paper. Under this heading may be mentioned also the importance of the use of dyes which possess considerable affinity for vegetable fibers. It is not practicable to enumerate the agents which should be employed in experiments to ascertain the resistance of a given dye to erasure, as light, heat, and all of the solvents and reagents known to the chemist are available for the use of persons who might desire them for use in assisting them in making fraudulent erasures.

For the purpose of canceling postage stamps, it is necessary that the canceling marks be substantially indelible, because the inks used in printing many of the stamps are very resistant. Stamping inks used for other purposes, however, do not require absolute indelibility.

In making the tests use several layers of blotting paper as a pad, pour on this a small quantity of the ink and distribute carefully; see that all excess has been absorbed by the pad before using the stamp. Make a sufficient number of impressions at one time to suffice for all tests and leave some in reserve. Having made the impressions, arrange them in groups according to the color and kind of ink, and rank them according to the following scheme:

1. Of highest rank.
2. Very good, but not of the best.
3. Good.
4. Fair.
5. Poor.

Having exposed the impressions to the various reagents, as described herein-after, each sample is again rated according to the effect of the reagents, as follows:

1. Unaffected.
2. Slightly affected.
3. Much affected.
4. Almost effaced.
5. Effaced.

The wet reagents used are pure water, water with the addition of 10 per cent of strong ammonia (sp. gr. 0.90), pure alcohol (95 per cent), alcohol with the addition of 10 per cent of strong ammonium hydroxid, 2 per cent hydrochloric acid, and 200th-normal bleaching powder. Expose each impression in a small Erlenmeyer flask to about 50 cc of the reagent for 24 hours, noting its appearance at the end of 15 minutes, 1 hour, and 24 hours. Then rinse dry and rate.

For the sunlight test expose impressions under glass for 10 days to direct sun, rating at the end of the third, seventh, and tenth days. The tests with reagents are considered of less use than the other tests, and are not always applied.

RUBBER-STAMP INKS.

1. Preparation and Care of Sample.

The precautions given in regard to the care of samples of inks made with an oil base should be observed.

2. Change of Weight on Exposure to Air.

This determination should be conducted in the manner described for the determination of volatile matter in inks made with an oil base. Rubber-stamp inks, however, gain or lose in weight according to the constituents used in their manufacture and according to atmospheric conditions. A rubber-stamp ink should not, however, undergo very much greater changes in weight when exposed to the air under given conditions than diluted glycerin containing 75 per cent of glycerin and 25 per cent of water by volume.

3. Penetrating Power.

This test should be conducted in the manner described for inks made with an oil base.

4. Sedimentation Test.

This test should be conducted as described for inks made with an oil base, with the exception that the portions of ink should be diluted with water instead of with organic solvents.

5. Determination of Lampblack and Other Constituents.

A scheme of analysis similar to that described for inks made with an oil base should be employed. Some experiments will be necessary in most cases to ascertain the proper solvent to be used in the case of each sample of ink to be examined. Alcohol, however, will generally be found to be satisfactory for rubber-stamp inks. This test is difficult and can not be carried out without a slight loss. To make the loss as small as possible use a very thick felt of asbestos and make the filtration continuous—never allow the gooch to run empty; if it does run empty, it is generally better to begin all over again.

6. Resistance to Light and Reagents.

The remarks made in regard to the investigation of the resistance of cancellations made with oil inks apply in general to canceling and other inks for use with rubber stamps.

MATERIALS USED FOR THE MANUFACTURE OF CANCELING AND OTHER STAMPING INKS.

1. Volatility and Penetrating Power.

The methods which have been described above will be found useful in determining the suitability of liquids for use as bases or constituents of bases of canceling and other stamping inks.

2. Sedimentation Test.

A modification of the sedimentation test described may be employed with good results for the purpose of ascertaining the suitability of lampblack and other pigments for use in the manufacture of canceling and other stamping inks. The results, of course, are mainly of value for purposes of comparison.

The conditions of the test may be modified to suit the purposes of the investigation and the character of the materials to be compared. The writer has obtained good results in the comparison of lampblacks and other blacks rich in uncombined carbon by the following method, which was so planned that the results might be applied to stamping inks made with either a water-soluble base or an oil base:

Mix 0.5 gram of the black to be tested in a mortar with dilute glycerin (87.5 cc of glycerin diluted with water to 1 liter). Rinse the mixture into a 100 cc Nessler cylinder and dilute to the 100 cc mark, using the same dilute glycerin. After having prepared a series of tubes, each containing a portion of one of the blacks to be tested, close each tube with a cork and shake thoroughly each tube successively, performing the operation as quickly as possible in order that the time of settling may be approximately the same in the case of each sample. Allow the cylinders to stand at rest in a place free from jar, and record from time to time the height of the sediment formed by the deposition of the blacks. When submitted to this test, a black which is suitable for the manufacture of a canceling or stamping ink should occupy a volume of not less than 25 cc when the sediment has stopped settling.

3. Ash, etc.

Blacks, dyes, and other substances used for the manufacture of canceling and other stamping inks should be carefully examined to insure the absence of considerable percentages of substances which are not essential to the production of an ink of good quality. It can generally be assumed that the presence of considerable quantities of any substance which does not actually contribute to the desirable qualities of the ink will detract therefrom. Black pigments rich in carbon of high specific gravity due to the presence of a large percentage of ash are highly unsuitable for the manufacture of stamping inks. Only the concentrated brands of coal-tar dyes should be used, unless the substances with which the less concentrated are diluted have been found to actually contribute to the working qualities of the ink to be produced.

MISCELLANEOUS.

GLUE.

Chemical analysis gives little information in regard to the value of glue. The chemical determinations are of more use in deciding as to whether a delivery is the same as a sample submitted than in deciding which is the best of a series of samples. Fernbach [a] says "save for alkalinity or acidity the chemical properties of glue are not factors in rational systems of test." In determining whether specifications have been complied with in making inking pads chemical tests are again of use.

1. Moisture.

Heat 3 grams of the finely divided sample for 2 hours in an oven at 105° to 110°C. It is important to use about the same quantity each time. Fernbach states that a good glue should contain not less than 8 nor more than 16 per cent of moisture.

2. Ash.

The sample used for the moisture determination may be ashed. Care is necessary in the ignition, which should be carried out at as low a temperature as possible. The ash should vary from 1.5 to 3 per cent. The condition of the ash gives some clue as to the origin of the glue. If the ash fuses, gives a neutral reaction, and contains traces of phosphates and chlorin it indicates a bone glue. The ash of a hide glue does not fuse, is slightly alkaline, and does not contain chlorids and phosphates. [b]

3. Reaction.

Test the solution in water with litmus paper. A quantitative determination is seldom of use. [c]

4. Gelatin.

A satisfactory approximation of the gelatin content is obtained by determining the nitrogen and multiplying by 5.56.

5. Water Absorption.

Place 10 grams of the sample, preferably in sheet form, in a weighed 400 cc beaker, pour 200 cc of water at 15° C. on the glue, cover the beaker, and let it stand for 24 hours in a refrigerator where the temperature is kept from 14° to 18° C. Then pour off the water and weigh the remainder. With ground glue some difficulty may be experienced in decanting the water; this is sometimes avoided by using a cage of fine wire gauze or a piece of bolting cloth to hold the ground glue. The temperature at which the water absorption is determined may be varied, but the figures obtained at one temperature are not to be compared with those at another. The determination can not be carried out on most glues at temperatures much above 20° C.

6. Viscosity.

Soak 50 grams of glue in 250 cc of water (at 20° C.) over night. Then dissolve by warming, not over 60° C., transfer to a 500 cc flask, dilute to the mark at 30° C., strain through bolting cloth into a somewhat larger flask, heat to

---

[a] Glues and Gelatine, p. 4.
[b] Ibid., pp. 59–61.
[c] Ibid., pp. 61–63.

60° C., cool to 30° C., and determine the viscosity immediately by the Engler method at 30° C. (The Bureau of Chemistry instrument requires 51.4 seconds to empty 200 cc water at 20°.) Concordant results can not be obtained by running the same solution a second time through the viscosimeter, the solution flowing faster each time. Fairly good results, however, can be obtained by heating the solution again to 60° C. and cooling to 30° C. When the size of the sample will permit, make up enough solution to run duplicates.

7. Jelly Strength.

This is one of the most important tests. Fernbach states that no apparatus gives as reliable results as the simple testing of the jelly by the finger. This, however, is an unsatisfactory method when only occasional samples of glue are examined. Place a 10 per cent solution of the glue in a narrow 300 cc beaker in a refrigerator for 24 hours at a temperature between 14° and 18° C. Remove the upper layer with a razor or sharp knife and determine the strength by the shot test as formulated by Lipowitz,[a] and modified by Fernbach, setting the beaker in a pan of water at 15° C. while making the test.

8. Melting Point of Jelly.

This determination is best made according to Cambon's fusiometer [b] method. The apparatus used in the Bureau of Chemistry is only a very slight modification of Cambon's, and consists of a metal cup (a ferrule) 22 mm high, 17 mm in diameter at the top, and 15 mm in diameter at the bottom, weighing 7 grams, and a glass tube 9 mm in diameter, and 160 mm long with the lower end sealed. Weigh accurately 2 grams of glue, place in a test tube with exactly 8 cc of water, cork, and allow to stand over night. Then dissolve the glue by holding the tube in warm water, not over 60° C. By shaking the tube a homogeneous liquid is easily obtained. Place the metal cup on a horizontal surface, suspend the glass tube vertically at about the center of the cup, with the closed end approximately 1 mm above the bottom. Pour the glue solution into the cup and allow it to set. (This may be hastened by surrounding the cup with ice water.) Fill a 600 cc Jena beaker, 12 cm high and 9 cm in diameter, two-thirds full of water at 15° C., and set it in a pan of water at 40° to 42° C. The water level in the pan should be about 15 mm below that in the beaker. Clamp the glass tube in a vertical position at such a distance above the center of the beaker that the metal cup is submerged to about 1 mm from the top. Suspend a centigrade thermometer, graduated in tenths, close to the cup and note the temperature at which the cup drops. Good glues have a melting point above 30° C., while that of inferior grades is several degrees lower.

GLYCERIN.

As a rule, no determinations are necessary on glycerin except ash and specific gravity.

1. Ash.

Ignite 10 grams at a low temperature, either in the muffle or in a hood having a very good draft.

2. Specific Gravity.

Determine with a pyknometer at 15.6° C.

---

[a] Fernbach. Glues and Gelatine, p. 46.
[b] Küttner and Ulrich. Zts. öff. Chem., 1907, **13**: 121–126.

3. Refractive Index.

Determine with a Zeiss direct reading refractometer at 15° or 17.5° C. With a pure article the per cent of glycerin may be obtained from either the specific gravity or the refractive index.[a]

4. Chemical Method of Determining Glycerol.

In impure glycerin, such as soap lye, a determination by physical methods is, of course, not reliable. For some mixtures, containing other reducing bodies, there is no really good method. When a chemical method is necessary, and sugar and other organic compounds are absent, Hehner's bichromate method is probably as satisfactory as any available. Place the crude glycerin (about 1.5 grams), or a corresponding amount of soap lye, from which all fatty acids have been removed, in a graduated 100 cc flask, dilute slightly, add some oxid of silver, allow to stand 10 minutes, and add a slight excess of basic lead acetate. Make up to the mark, filter through a dry paper, and place 25 cc of the filtrate in a perfectly clean beaker. Add first an accurately measured amount (40 to 50 cc) of a solution of bichromate (made by dissolving 74.86 grams of potassium bichromate in water and diluting to 1,000 cc, the exact strength being then determined against pure iron or ferrous ammonium sulphate), then 15 cc of strong sulphuric acid. Cover the beaker and heat for two hours in boiling water; then cool. Add an excess of standard ferrous ammonium sulphate solution and titrate back with a standard bichromate solution containing 7.486 grams per liter. (The ferrous ammonium sulphate solution should contain about 240 grams per 1,000 cc.) One cubic centimeter of the strong bichromate solution corresponds to 0.01 gram of glycerol.

INKING PADS.

The material used in these pads is printers' roller composition, being composed of glue and glycerin generally with a small amount of borax added.

1. Sampling.

Weigh the whole pads, remove the felt and weigh again. Cut the pad in quarters and when only one pad is furnished cut up two opposite quarters into very small and uniform pieces. When several pads are in one sample, take smaller segments from each pad. It is very important that the samples be all cut to a uniform size—cubes about 2 mm on each edge.

2. Moisture.

Cover the bottom of a small, flat-bottomed aluminum dish (2.5 inches in diameter, and five-eighths of an inch high) with freshly ignited sand, weigh, distribute over the sand from 1.5 to 2 grams of the fine pieces of pad, weigh accurately, and heat for 2 hours in a water oven, cool in a desiccator, and weigh. Duplicates should agree within 0.3 per cent.

3. Ash.

Char carefully 10 grams of the sample in a 100 cc, or larger, platinum dish, extract with water, filter, burn filter and carbonaceous matter, add water extract, evaporate, and heat to low red heat.

---

[a] Lewkowitsch, Oils, Fats, and Waxes, 1904, **2**: 1105.

4. Borax.

To 30 grams of the sample in a large platinum dish, add 5 cc of a 20 per cent solution of sodium hydroxid and 10 cc of a saturated solution of barium hydroxid, char, extract with water and dilute hydrochloric acid, ash the residue, and extract the ash with dilute hydrochloric acid. Transfer to a 250 cc graduated flask, add about 0.5 gram of calcium chlorid and a few drops of phenolphthalein, then a 10 per cent solution of sodium hydroxid until slightly alkaline, followed by 25 cc of lime water. Make up to mark, mix, filter through a dry paper and titrate 100 cc. with half-normal sulphuric acid until the pink color disappears, then add methyl orange and continue the addition of half-normal sulphuric acid until the yellow is changed to pink. Add fifth-normal sodium hydroxid until the solution is exactly neutral to methyl orange; boil until all carbon dioxid is driven off, cool, add almost enough mannite to saturate the solution. Add phenolphthalein and titrate with fifth-normal sodium hydroxid.

One cubic centimeter of fifth-normal sodium hydroxid corresponds to 0.0191 gram $Na_2B_4O_7 \cdot 10H_2O$; 0.0101 gram $Na_2B_4O_7$; 0.0124 gram H_3BO_3; 0.007 gram B_2O_3.

5. Gelatin.

Determine the nitrogen and multiply by 5.56. From the moisture and gelatin, if these values are known for the glue originally used, an approximation of the amount of glue used in making the pad can be calculated. The ash is only a rough check as some of the boric acid is lost on burning.

LUBRICATING OILS.

1. Specific Gravity.

Determine with a pyknometer at the temperature given in the specification.

2. Flash and Fire Points.

Follow the method given under linseed oil, page 5.

3. Viscosity.

Use the Engler instrument unless some other apparatus is named in the specification.

4. Ash.

Burn 10 grams of the oil at as low a temperature as possible. Determine the reaction of the ash with litmus paper. The amount of ash should be very small and neutral unless the oil contains soap, when the reaction will be alkaline.

5. Reaction of Oil.

Heat about 20 grams of the oil with 50 cc of water, draw off the water and test its reaction with litmus. If the reaction is acid it is probably due to sulphuric acid; test with barium chlorid.

6. Action on Copper.

Spread some of the oil on a bright polished piece of copper and expose to the air for 24 hours. The copper should not corrode or turn green.

7. Tarry and Suspended Matter.

Place 5 cc of the oil in a 100 cc stoppered cylinder, add 95 cc of gasoline, shake well, and allow to stand 15 minutes. No precipitate should appear.

8. Cold Test.

Warm the oil up to 80° C. and if it contains any solid particles keep at 80° until they are completely melted. Put 50 cc of the oil in a dry, 4-ounce, wide-mouthed bottle, provided with a stopper through which passes a thermometer. Place in a freezing mixture and stir gently with the thermometer until the oil is frozen, insert the cork, and leave the bottle in the freezing mixture for an hour. Then remove from the bath, wipe dry, and place in a beaker packed with dry asbestos to insulate the sides of the bottle. Break up and stir the oil with the thermometer; invert the bottle at every degree of rise in temperature, and note the temperature at which the oil will flow from one end of the bottle to the other in 15 seconds. For the freezing mixture for temperatures above 2° C., use ice and water, for lower temperatures use ice and salt, or if necessary crystallized calcium chlorid and snow.

9. Volatility.

Heat from 0.5 to 1.5 grams of oil in a flat-bottomed dish in a bath at the temperature of boiling water for 4 hours.

10. Fatty Oil.—Qualitative Test.

Heat 4 or 5 cc of the oil in a test tube with a piece of caustic soda (solid) for 15 minutes at a temperature of 230° to 250° C. Allow to cool. The presence of fatty oil is indicated by the gelatinization, complete or partial, of the contents of the tube.

11. Quantitative Determination.

In the presence of large quantities of mineral oil, saponification with alcoholic potash takes a long time, since the mineral oil prevents the potash coming in contact with the fatty oil. Schreiber's method [a] gives good results in a short time. Weigh 5 grams of the oil in a 200 cc Erlenmeyer flask, add 25 to 50 cc of half-normal alcoholic potash and sufficient benzol (C_6H_6) to dissolve the oil when warmed (generally 25 cc is enough, but with heavy cylinder oils as much as 50 cc may be necessary; in this case it is well to add 25 cc of neutral alcohol). Connect the flask with a 3-foot condenser and set it on the iron plate that forms the top of the steam bath, so that the steam will not strike it directly, and regulate the heat so that the condensing liquid will not be forced to the top of the condenser. In this way the contents of the flask can be boiled without apparently losing any of the solvent. Boil for 30 minutes. Cool, add phenolphthalein, and titrate the excess of potassium hydroxid with half-normal sulphuric acid. On adding the acid the liquid separates into two layers and the change in color can be seen in the lower layer; the titrating, however, must be conducted slowly. Subtract the cubic centimeters of sulphuric acid from the amount used on blanks and calculate the saponification number. For all practical purposes 195 may be considered as the saponification number of the fatty oils used in lubricating oils and hence if S equals the determined saponification number, 100 S divided by 195 equals the percentage of fatty oil present.

---

[a] J. Amer. Chem. Soc., 1907, **29** : 74.

When the oil is very dark, or when soaps are present, it may be necessary to determine the hydrocarbon oils directly. For this purpose saponify as described, cool, add 25 cc of benzol, transfer to a separatory funnel, add 100 cc of water, shake, allow to settle, draw off the water layer, and wash the benzol three times with 100 cc of water; wash the soap solution with three portions of 50 cc of benzol, evaporate off the benzol solution, and weigh the nonvolatile hydrocarbon oils.

12. Acid Number.

See linseed oil, page 7.

13. Rosin Oil.

See linseed oil, page 8.

PHENOLIC DISINFECTANT.

The phenolic soap mixtures can generally be identified as they form an emulsion with water. They consist of phenolic soaps and hydrocarbon oils and are quite variable in composition. The following scheme for analysis is only a slight modification of that given by Allen.[a] The only important modification consists in the recovery of light hydrocarbons, which by Allen's process would be lost.

1. Volatile Hydrocarbons.

Mix the sample thoroughly, weigh a portion of somewhat more than 100 grams in an Erlenmeyer flask with a funnel. Pour about 100 grams into a distilling flask of 150 to 200 cc capacity, using the funnel to prevent the disinfectant from getting on the neck of the flask, weigh back the Erlenmeyer flask and the funnel, and get the exact weight by difference. The delivery tube of the distilling flask should be bent so that it can connect with a small vertical condenser; all connections are made of cork. Pass the thermometer through the cork of the distilling flask and heat the flask in a paraffin bath, slowly and carefully, not exceeding 130° C., for one and one-half hours, or until the substance becomes solid or ceases to give off volatile matter. The receiver is a small separatory funnel with a short tube, the tube of the condenser being connected with it by a cork having a groove cut into it for the free passage of air. The funnel is weighed empty, and again with the total volatile liquid; then the water is drawn off and the remaining liquid weighed as volatile hydrocarbon.

2. Pyridin.

Dissolve the residue in the distilling flask in water, it is usually necessary to add 60 cc of water; heat slowly to avoid foaming and leave the flask in the steam bath for about an hour. Wash the soapy solution into a 500 cc separatory funnel, add dilute sulphuric acid (1 : 3) until the liquid is distinctly acid to litmus, cool, shake with ether, drain off the acid layer and shake it twice with additional portions of ether, wash the ether twice with water, unite the acid water solutions, transfer to a large round-bottomed flask, and render distinctly alkaline with sodium hydroxid, but avoid a great excess of alkali as it will cause foaming. Use a spray trap and a large condenser. In all distillations tie the stopper in the flasks and condensers as they are liable to be blown out, and distil in a current of steam until all of the pyridin has passed over. This is usually a tedious operation but in most cases the pyridin can be driven over in the first 600 or 700 cc. To ascertain whether all of the

---

[a] Commercial Organic Analysis, 3d ed., **2** (2) : 262.

pyridin has come over, mix 10 cc of the distillate with 10 cc of a solution of 1 drop of half-normal sulphuric acid in 50 cc of water colored with methyl orange. The 10 cc of distillate should not change the color of the solution. Transfer the distillate to a 1,000 cc graduated flask, add an excess of half-normal sulphuric acid, fill to the mark, mix, and titrate aliquots back with fifth-normal sodium hydroxid using methyl orange. From the amount of half-normal sulphuric acid neutralized, calculate the percentage of pyridin (1 cc of half-normal sulphuric acid corresponds to 0.0395 gram of pyridin).

3. Heavy Hydrocarbons.

The ethereal layer above the acid solution in which the pyridin is, contains hydrocarbons, phenols, and fatty and resin acids. Add a 25 per cent solution of sodium hydroxid in amount sufficient to combine with all the fatty and resin acids and phenols, shake, add water to dissolve the soaps, shake again, and allow to settle. It will frequently be observed that there are not two layers but three, and care must be taken to distinguish between the dark ethereal layer and the intermediate dark alkaline layer below it. Draw off the liquid underneath the ether, shake out twice again with ether, wash all ether portions three times with water, unite the ether solutions in a weighed Erlenmeyer flask, distil off the ether, dry for three-quarters of an hour on a steam bath, wipe out the moisture from the neck of the flask, and weigh as heavy hydrocarbons. Concordant results can not be obtained by drying to constant weight, hence it is always much better to leave the Erlenmeyer flask on the steam bath exactly three-quarters of an hour after distilling off the ether.

4. Phenols.

Heat the alkaline liquid separated from the heavy hydrocarbons on the steam bath to drive off the ether, transfer it to a round-bottomed flask, make distinctly acid with sulphuric acid (1:3) and distil in a current of steam until no more oily drops pass over (do not use a spray trap); to the distillate add an excess of sodium hydroxid, evaporate to about 20 cc, transfer to a narrow graduated stoppered cylinder, acidify with sulphuric acid (1:3) keeping it cool, mix, allow to settle over night, and measure the layer of phenol. The volume in cubic centimeters multiplied by 1.05 gives the number of grams of phenols.

5. Fatty and Resin Acids.

Cool the residue in a distilling flask, extract with ether, distil off the ether, dry on a steam bath three-quarters of an hour, cool, and weigh as fatty and resin acids.

6. Other Tests.

Ash a 10 gram portion of the disinfectant and determine the alkalinity of the ash, and whether the alkali is soda or potash.

In determining the relative values of disinfectants of this class, the sample should be submitted to a bacteriological test. In the absence of such a test the substance may be graded by the sum of the percentage of phenols and pyridin. This is, of course, only a general approximation, as the hydrocarbons and soaps doubtless have some germicidal action.

SOAP.

1. Sampling.

It is somewhat difficult to secure a fair sample from a cake of soap as the moisture content of the outer layer may be very different from that of the interior of the cake. Weigh the whole cake, cut it in two in a diagonal direction, and cut from one of these fresh surfaces in thin layers a sufficient quantity for all determinations, taking care to cut entirely across so as to get a fair proportion of the outer and inner parts. When the cake is not too soft it is sometimes a good plan to run the whole cake through a meat chopper and reduce it all to fine particles. By running through the chopper several times a homogeneous sample is obtained. Preserve the sample in a tightly stoppered bottle and weigh the different portions required as soon as possible.

2. Moisture.

The determination of moisture is at best unsatisfactory and it is better to include it in the " Undetermined." If a determination is required, heat 2 grams of the finely shaved soap for 2 hours in an oven at 105° C. The loss is considered as water, though, of course, this is not accurate, as volatile oils may constitute part of the loss, and on the other hand, all of the water may not be driven off, and if the soap contains free alkali, carbon dioxid will be absorbed from the air. This last source of error may be avoided by drying in vacuo.

Fahrion's method [a] is much quicker and probably as exact. The author states that it gives results within 0.5 per cent of the truth. For this method have a supply of oleic acid which has been heated to 120° with stirring until all of the water is driven off and preserved in a well-stoppered bottle. Weigh from 2 to 4 grams of the soap in a platinum dish, add three times its weight of oleic acid, and weigh again. Heat the dish cautiously with a small flame until all of the water is driven off and all of the soap is dissolved, being careful not to heat enough to decompose the acid. At the moment when all of the water is driven off the soap forms a clear solution with the acid if there are no fillers present. Cool in a desiccator and weigh. This determination does not require more than fifteen minutes.

3. Insoluble Matter.

Dissolve 5 grams of soap in hot water (use about 75 cc). Filter on a Gooch or weighed paper and wash with hot water; dry at 105° C., weigh, and calculate the percentage of total insoluble. Ignite the residue and calculate the percentage of insoluble mineral matter.

4. Total Fatty Matter.

To the filtrate from the insoluble matter add 20 cc of half-normal sulphuric acid, heat on the water bath until the fatty acids have collected in a clear layer on top, cool in ice water, remove the layer of fatty acids, and wash with water; then heat again with water, cool, remove fatty layer, wash with ice water, dry with filter paper, unite the acid liquids, transfer to a separatory funnel, and shake out with two portions of 50 cc each of gasoline; wash the gasoline twice with 20 cc of water. Evaporate off the gasoline, add the cake of fatty acids, etc., dry at 100°, and weigh as total fatty matter. This may represent fatty acids, uncombined fat, rosin and hydrocarbons.

[a] Zts. angew. Chem., 1906, **19**: 385.

5. Total Alkali.

Heat the acid liquid obtained from the determination of total fatty matter to drive off traces of gasoline, cool, add methyl orange, and titrate the excess of acid with fifth-normal alkali. From this titration calculate the amount of acid neutralized by alkali in soap and figure to percentage of sodium monoxid.

A more rapid method is to ash the soap, dissolve the ash in water, and titrate. This method gives good results in the absence of silica or other mineral fillers, but can not be used in their presence.

6. Free Alkali.

(a) ALCOHOLIC METHOD.

Treat the freshly cut surface of the soap with a few drops of an alcoholic solution of phenolphthalein; if it does not turn red it may be assumed that free caustic alkali is absent. If free alkali is present, dissolve 2 grams of the soap in 100 cc of neutral alcohol (heat is necessary to complete the solution), filter from the undissolved sodium carbonate, etc.; wash with alcohol, add phenolphthalein, titrate with standard acid, and calculate to per cent of free alkali as sodium hydroxid. Should the alcoholic solution be acid instead of alkaline, titrate with standard alkali and calculate the percentage of free fatty acid as oleic acid.

Wash the portion insoluble in alcohol with water, add methyl orange to the washings, and titrate with half-normal sulphuric acid. Calculate to percentage of sodium monoxid present as carbonate, or possibly as borate or silicate. If borax is present boil off the carbon dioxid after neutralizing exactly to methyl orange; cool, add mannite and phenolphthalein, and titrate the boric acid with standard alkali.

(b) DEVINE'S METHOD.

The alcohol method of determining free alkali is open to the objection that if the soap contains free alkali and free fat also, by the heating with alcohol the fat will be partly or completely saponified and the free alkali may not be obtainable. Devine's method [a] avoids this danger. For this method three standard solutions are used:

1. Tenth-normal hydrochloric acid.
2. Tenth-normal caustic soda or potash in alcohol.
3. Tenth-normal stearic acid in alcohol.

Solution No. 1 is used to standardize No. 2; Nos. 2 and 3 should be titrated against one another warm, using phenolphthalein as indicator.

Weigh 2 grams of soap (which needs no drying) into a round-bottomed flask of about 300 cc capacity, and pour 50 cc of alcohol upon it. Run in sufficient tenth-normal stearic acid from a burette to neutralize the free alkali in 2 grams of the soap, add some phenolphthalein, and stopper the flask with a cork stopper through which passes a glass tube about 30 inches long and of about $\frac{1}{4}$ inch internal diameter, having the lower end ground to a point on a grindstone. The purpose of the tube is to serve as a reflux condenser. Place the flask and contents on a steam bath and heat for thirty minutes. At the expiration of this time the solution should be quite clear and show no alkali with the phenolphthalein. If the solution turns red during the boiling, showing that an insufficient quantity of stearic acid has been added at first, add more of that solution until the color disappears, then several cubic centimeters in ex-

---

[a] J. Amer. Chem. Soc., 1900, **22**: 693.

cess, and heat twenty minutes longer. Remove the flask from the bath and, after cooling it a few minutes, titrate with tenth-normal caustic soda. The difference between the number of cubic centimeters of stearic acid solution added and the number of cubic centimeters of caustic soda used to neutralize it, is equivalent to the total free alkali present.

While the first flask is heating, weigh in a similar flask 2 grams of soap, add 50 cc of alcohol, and place on the steam bath. When the first test is finished, calculate roughly the total alkali, assuming the total quantity to be carbonate. Now add to the second flask sufficient 10 per cent barium chlorid solution to precipitate the alkali found,[a] heat a few minutes, add phenolphthalein, and titrate with tenth-normal stearic acid. The titration must take place slowly and with thorough agitation of the liquid because the sodium or potassium hydroxid reacts with the barium chlorid added and forms sodium chlorid and barium hydroxid. The latter is not very soluble in the alcoholic liquid, and sufficient time and pains must be taken to insure its complete neutralization by the stearic acid. Make a blank test on 50 cc of the alcohol, since this frequently contains carbon dioxid, and add the amount of tenth-normal caustic soda necessary to neutralize the free acid in this quantity of alcohol to the reading of the stearic acid burette in the second test. This corrected reading gives the number of cubic centimeters of tenth-normal stearic acid used to neutralize the caustic alkali in 2 grams of soap. The difference between the total alkali found and the caustic soda will, of course, give the carbonate. For example: To 2 grams of soap and 15 cc of tenth-normal stearic acid add 3.2 cc of tenth-normal caustic soda to neutralize. Then 15 cc − 3.2 cc =11.8 cc of tenth-normal stearic acid equivalent to total free alkali.

To neutralize the caustic soda in the sample treated with barium chlorid 4.1 cc of tenth-normal stearic acid was required. Fifty cubic centimeters of the alcohol used required 0.2 cc of tenth-normal caustic soda, hence the total is 4.3 cc. Since it requires 4.3 cc of tenth-normal stearic acid to neutralize free caustic alkali, 11.8 cc − 4.3 cc = 7.5 cc of tenth-normal stearic acid required to neutralize the carbonated alkali.

One cubic centimeter of tenth-normal stearic acid = 0.004 gram of caustic soda or 0.0053 gram of sodium carbonate. These figures calculated to percentage would be: 0.86 per cent of caustic soda and 1.99 per cent of sodium carbonate.

It is to be noted that a rubber stopper can not be used in the flasks used for dissolving the soap on account of the sulphur in the rubber which decolorizes an alcoholic solution of phenolphthalein. The method is applicable to all soaps that do not contain fillers which react with the standard solutions employed.

7. Unsaponified Matter.

Dissolve 5 grams of soap in 50 cc of 50 per cent alcohol; if any free fatty acids are present add just enough standard alkali to neutralize them and wash into a separatory funnel with 50 per cent alcohol. Extract with 100 cc of gasoline (B. P. 50°–60°). Wash the gasoline with water, evaporate, and weigh as unsaponified. This may consist of fat that has not been converted into soap or of hydrocarbon oils.

8. Rosin.

If much unsaponified matter is present, prepare dry fatty and rosin acids from the portion from which the unsaponified matter has been removed. Dis-

---

[a] One cubic centimeter of tenth-normal stearic acid corresponds to 0.0122 gram $BaCl_2$ $2H_2O$ or 0.122 cc of a 10 per cent barium chlorid solution.

solve 3 grams of the dry mixed acids in 25 cc of absolute alcohol in a 100 cc stoppered flask, place the flask in cold water and shake; add 25 cc of absolute alcohol saturated with dry hydrochloric acid, shake occasionally, and let the action go on for 20 minutes; then add 10 grams of dry granular zinc chlorid, shake, and allow to stand for 20 minutes. Pour the contents of the flask into 200 cc of water in a 500 cc beaker, and rinse out the flask with dilute alcohol. Put a small stick of metallic zinc in the beaker and boil off the alcohol. Cool, transfer to a separatory funnel, extract with gasoline, wash the gasoline until free from hydrochloric acid, distil off the gasoline, dissolve in neutral alcohol, and titrate with standard alkali using phenolpthalein as indicator. (One cubic centimeter of tenth-normal alkali corresponds to 0.346 gram of rosin.) The rosin may be determined gravimetrically by washing the gasoline extract with water. It is not necessary to wash absolutely free from acid. Then treat the extract in the funnel with a solution of 5 grams of potassium hydroxid and 5 cc of alcohol in 50 cc of water. Upon shaking, the rosin is rapidly saponified and the two layers separate well. Draw off the rosin soap, wash the gasoline once with water, add the washings to the soap solution, add an excess of acid, extract the rosin with gasoline, evaporate the gasoline, and weigh the rosin.

9. Silica and Silicates.

Insoluble silicates, sand, etc., are present in the insoluble; but sodium silicate fillers will only show by forming pasty liquids. When sodium silicate is suspected, ash the soap (10 grams), add an excess of hydrochloric acid to the ash, evaporate to dryness; add hydrochloric acid and again evaporate to dryness; cool, moisten with hydrochloric acid, dissolve in water, filter, wash, evaporate the filtrate to dryness, and again take up with hydrochloric acid and water, filter, and wash. Unite the precipitates, ignite, and weigh as silicon dioxid; calculate to sodium silicate ($Na_2Si_4O_9$). If metals other than the alkalis are suspected, the filtrate from the silica determination may be examined.

10. Glycerin.

Dissolve 20 to 25 grams of soap in hot water, add a slight excess of sulphuric acid and heat on a water bath until the fatty acids separate in a clear layer. Remove the fatty acids and filter the acid solution into a graduated flask. Remove the chlorids and the soluble fatty acids by adding crystals of silver sulphate, cool, make up to the mark, mix, allow to settle, filter through dry paper, take an aliquot corresponding to 5 grams of soap, and determine by Hehner's bichromate method (see under Glycerin, p. 39). This method can not be used when sugar is present as the sugar would also reduce the bichromate. When sugar is present remove the fatty acids as described. Neutralize an aliquot with milk of lime, evaporate to about 10 cc, add 2 grams of sand and milk of lime containing about 2 grams of calcium hydroxid, and evaporate almost to dryness. Treat the moist residue with 5 cc of 96 per cent alcohol, rub the whole mass into a paste, heat the mixture on a water bath stirring constantly, and decant the liquid into a 250 cc flask, wash the residue five or six times with small portions of alcohol, cool the contents of the flask to 15°, fill to the mark with 96 per cent alcohol, mix, and filter through a dry paper; take 200 cc of the filtrate, evaporate to a sirupy consistency on a water bath, transfer to a stoppered cylinder with 20 cc of absolute alcohol, add three portions of 10 cc each of absolute ether, mixing after each addition; let stand until clear, pour off through a filter, and wash the

cylinder on the filter with a mixture of two parts of absolute alcohol and three parts of absolute ether. Evaporate to a sirup, dry for one hour at the temperature of boiling water, weigh, ignite, and weigh again. The loss multiplied by 5/4 is the weight of the glycerin in the aliquot taken. Instead of weighing the glycerin it can be titrated after driving off the alcohol and ether.

11. Sugar.

Dissolve 5 grams of soap in water, add an excess of hydrochloric acid, heat on a steam bath for 30 minutes, cool, separate the fatty acids, and make up to a definite volume. Add an aliquot, depending upon the amount of sugar supposed to be present, to 50 cc of a mixed Soxhlet solution, make the total volume 100 cc, heat to boiling, boil two minutes, filter on a weighed gooch, wash with water, then with alcohol and ether, dry at 100° for 30 minutes, cool, and weigh the cuprous oxid. Calculate the percentage of sugar as invert sugar according to Munson and Walker's tables.[a]

---

[a] J. Amer. Chem. Soc., 1906, **28** : 663–686.